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SPACE REACTOR MATERIALS
MATERIALS DEVELOPMENT ORGANIZATION

SPACE MATERIALS MEMORANDUM

TITLE: Initial Assessment of Environmental Barrier Coatings for the Prometheus Project

AUTHOR: M.J. Frederick

Abstract

Depending upon final design and materials selections, a variety of engineering solutions may need to be considered to avoid chemical degradation of components in a notional space nuclear power plant (SNPP). Coatings are one engineered approach that was considered. A comprehensive review of protective coating technology for various space-reactor structural materials is presented, including refractory metal alloys [molybdenum (Mo), tungsten (W), rhenium (Re), tantalum (Ta), and niobium (Nb)], nickel (Ni)-base superalloys, and silicon carbide (SiC). A summary description of some common deposition techniques is included. A literature survey identified coatings based on silicides or iridium/rhenium as the primary methods for environmental protection of refractory metal alloys. Modified aluminide coatings have been identified for superalloys and multilayer ceramic coatings for protection of SiC. All reviewed research focused on protecting structural materials from extreme temperatures in highly oxidizing conditions. Thermodynamic analyses indicate that some of these coatings may not be protective in the high-temperature, impure-He environment expected in a Prometheus reactor system. Further research is proposed to determine extensibility of these coating materials to less-oxidizing or neutral environments.

1. Introduction

A variety of materials have been proposed for use in the Prometheus space reactor, including refractory metal alloys [molybdenum (Mo), tungsten (W), rhenium (Re), tantalum (Ta), and niobium (Nb)], nickel (Ni)-base superalloys, and silicon carbide (SiC). These materials have been proposed for structural components in reactor cores, and other parts of a space power plant (SPP) based on the requirements of high temperature strength, creep resistance, manufacturability, neutronics, and environmental resistance. However, none of the materials (or their combinations) are without limitations in ambient environments proposed for space reactor systems. Use of refractory metal alloys raises a variety of concerns based on ductility loss due to interstitial embrittlement for Ta- and Nb-base alloys, and potential volatile oxide formation and subsequent mass loss for Mo alloys. These undesirable reactions stem from interactions with impurities that may be pre-existing in the He/Xe gas or through thermodynamic reactions with other materials in contact with the gas mixture, such as Ni-base superalloys, insulation

materials, carbon-carbon composites, alternator components, solid lubricants (fluorides and sulfides), and polymers. SiC has a well-known active oxidation regime in low oxygen potential environments that must be avoided. A solution to these issues may be found by use of environmental barrier coatings (EBCs) that would serve to isolate and protect these structural materials from adverse reactions with the surrounding material systems. Requirements for the coating material properties and microstructure will need to be as strict, if not stricter, than requirements for the base materials they are used to protect.

This report provides:

- A brief understanding of material interactions that have led to consideration of an EBC.
- Property requirements for an EBC.
- An overview of common coating techniques.
- A review of previous coating studies developed for structural materials under consideration.
- A discussion regarding applicability of coatings to notional Prometheus reactor environments.
- A proposal for future research to advance potential coating systems to a level of usefulness for Prometheus (core and plant).

2. Reasons for Investigation of Coatings

Proposed Prometheus reactor designs call for various levels of use of dissimilar materials connected by a common He-Xe gas loop. Proposed plant materials have focused on Ni-base superalloys and titanium alloys, but proposals for core structural materials include refractory metals, Ni-base superalloys, and SiC. For Nb and Ta alloys, the primary concern is severe interstitial embrittlement upon exposure to oxygen and carbon-containing gases. Thermodynamic data indicate carbon and oxygen can significantly lower their activity by transferring from the Ni-base superalloys to Ta and Nb alloys connected through a common He gas loop. Without gettering, coatings, or other engineered solutions, this process could result in catastrophic loss of mechanical strength in these refractory metal alloys as well as loss of creep strength in the Ni-base superalloys. Mo-base alloys can suffer from formation of volatile oxides which can lead to material recession over prolonged times. Also, oxygen segregation to Mo grain boundaries can lead to grain boundary embrittlement. SiC, while not prone to the large changes in mechanical properties as seen in refractory metal alloys, could suffer from material recession due to active oxidation within a He environment of reduced oxygen activity. Properly chosen EBCs is one approach to mitigate these materials degradation issues and allow retention of material properties of structural components within this environment through mission life.

3. Requirements for Environmental Barrier Coatings

A preliminary list of requirements and issues that must be addressed for any potential coating solution was developed:

1. Coatings must be sufficiently thick to successfully protect structural materials from undesirable environmental interactions occurring over proposed mission lifetimes.
2. EBCs must demonstrate phase stability over temperature ranges of operation. Any phase changes would likely cause unstable stress states and compromise coating integrity.

3. Coatings must be metallurgically stable with respect to any underlying substrate or other materials that are in thermodynamic communication*. Phase formation between coating and substrate material should be avoided.
4. Coatings must demonstrate adequate adhesion to substrate materials.
5. Coefficients of thermal expansion need to be closely matched between coating and substrate to prevent formation of high thermal stresses that could lead to film cracking or spallation. This may be addressed through proper alloying or tailoring the stress state of as-deposited coatings.
6. Microstructures must be tailored to eliminate any fast diffusion paths (i.e. columnar grain structure must be avoided).
7. Application of coatings should not expose substrate materials to adverse environmental contaminants.
8. Irradiation effects on any coating must be determined with respect to structural and phase stability and changes in environmental durability. Also, coatings choices must be factored into nuclear designs and radiological assessments.
9. Any coating material must have a suitably low vapor pressure to minimize sublimation and contamination of the working gas.
10. Coating materials must be thermodynamically stable with respect to the working gas and other materials in contact with the gas.
11. Coatings must possess self-healing properties and should be resistant to impacts, erosion, and abrasion.
12. Coatings must not degrade mechanical properties of the substrate alloy to a level that would preclude the material performing in a fashion consistent with meeting mission requirements.

4. Summary of Available Vapor Phase Coating and Film Technologies

A wide variety of technologies exist for vapor phase deposition of functional coatings. These technologies are primarily delineated by the nature of the physical process involved in coating growth. The two broad categories are physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD, a solid is transformed into a vapor or particulate stream that is carried to the substrate (or part) where it condenses and forms a coating. CVD is a deposition technology based on the interaction of two or more chemicals that are transported within the gas phase to a substrate (or part), where a chemical reaction takes place to form a desired film. A review of thin film coating technology can be found in reference [1]. For a review of non-vapor phase techniques (sol-gel, slurry, molten salt), the reader is referred to [2].

* Thermodynamic communication in this context refers to equilibrium-driven thermochemical reactions made possible through mass transport in a common gas loop.

4.1. PVD

4.1.1.1. Sputter Deposition principles

Sputtering is a vacuum-based deposition process whereby material is ejected from a solid via a momentum transfer process. In short, a desired coating material (known as a target) is placed within a vacuum system which is then evacuated to its base pressure. An inert gas (generally argon) is then backfilled into the chamber, typically to a pressure in the range of 10^{-3} - 10^{-1} Torr. A glow discharge is then created within the inert gas, and inert gas ions are accelerated and collide with the target material thereby ejecting atoms of target material. These vaporized target atoms then condense upon a substrate creating a film. A simple method to create ion acceleration is to negatively bias a target material, therefore this technique is commonly referred to as cathodic sputter deposition. A schematic representation of a sputtering process chamber is shown in Figure 1.

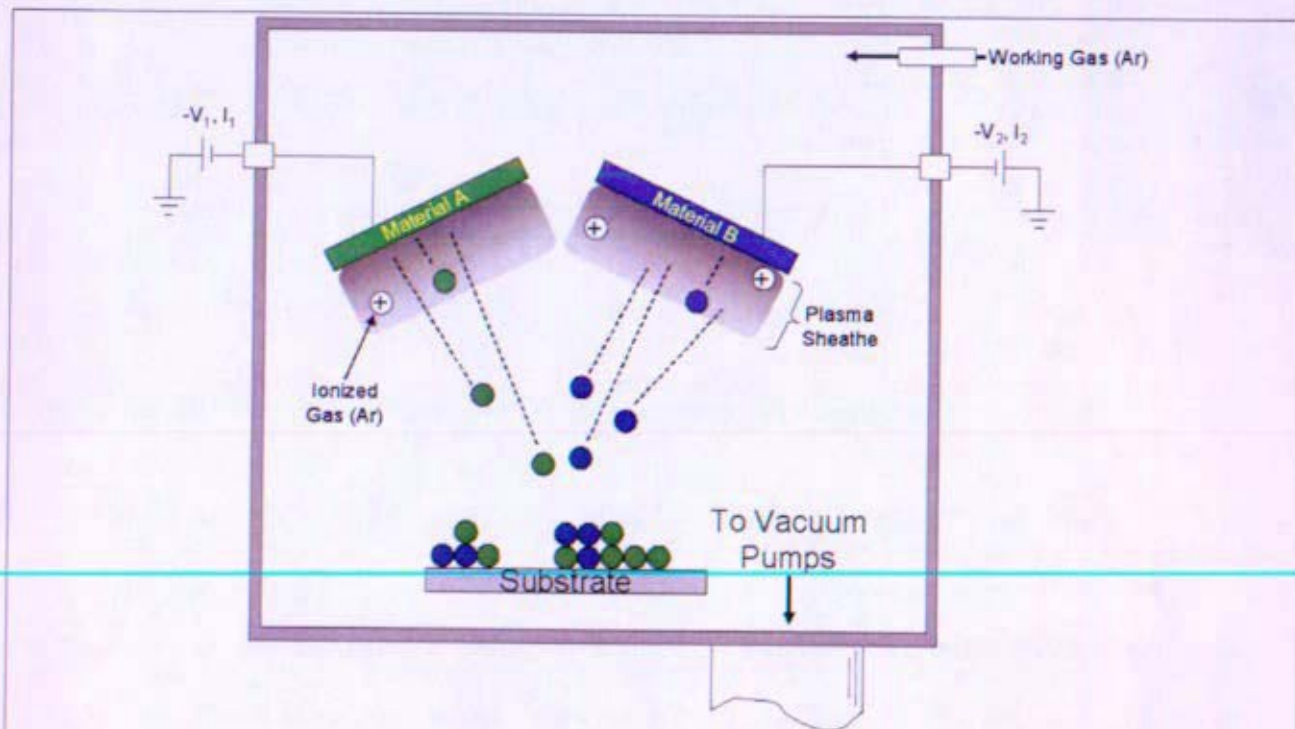


Figure 1: A schematic representation of the sputter deposition process. Here, two independently controlled target materials are being sputtered to form an alloy coating.

4.1.1.2. Sputter Deposition practice

In theory, any material can be sputtered, but in practice, sputter deposition is typically only used to deposit metals and conducting alloys. Difficulties arise with insulators because a surface charge will build up on the target that stops the sputtering process and can lead to electrical arcing within the vacuum system. In order to sputter deposit insulators, a radio frequency (RF) power supply must be used to prevent this charge build up, rather than a standard direct current (DC) configuration. While a common solution, RF is generally avoided due to slow deposition rates and problems with impurity incorporation into films. Because an RF bias of a target is alternated between anodic and cathodic, half the time the vacuum chamber is *acting as the*

target. This has lead to observations of iron incorporation from stainless steel vessel walls into insulator films.

Purity of sputtered films can be extremely high and is based on target purity, working gas purity, and base vacuum system pressure. Advantages of sputtering lie in the accurate control that can be exercised over film stoichiometry. Unlike other PVD methods, sputter deposited film stoichiometry is identical to target material stoichiometry. In thermal evaporation of alloys, film composition is limited/determined by the different vapor pressures of alloy constituents, but this is not a limitation for sputter deposition. If it is desired to study a range of alloy compositions, multiple targets can be placed within a single vacuum chamber and by varying biasing of each individual target, virtually any composition can be deposited.

Sputter deposition is a non-equilibrium process, so it is possible to deposit metastable phases not present in, or expected from, the equilibrium phase diagram. There are also a variety of advanced techniques available to control coating stress state (tensile to compressive), microstructure, and phase. However, like other PVD methods, sputter deposition is a line-of-sight method, i.e., a target must be within line-of-sight of any substrate. Therefore, it is not extendable to complex shapes with high aspect ratio features. It is also important to note that sputter deposition cannot match the fast deposition rates of evaporation as sputtering is limited by target thermal conductivity and how quickly heat can be removed.

For many years sputter deposition was the primary technique used by microelectronics companies to grow metal films used for interconnects in microchips. This technique is slowly being supplanted by CVD as line-of-sight issues become more critical. Sputter deposition is also used to deposit erosion resistant coatings on gun barrel interiors as well as hard coatings on tool bits.

4.1.2.1. Thermal Evaporation principles

Thermal evaporation is another vacuum-based deposition process where a source material is heated to create a vapor which then recondenses upon a substrate.[1] Depending on material properties, vapor is created either through vaporization or sublimation. Heat is provided by a number of different mechanisms including resistive heating, induction, or electron-beam. Resistive heating is generally used for low-melting point materials due to its relative technical simplicity. For higher temperature materials like refractory metals, most notably tungsten, e-beam evaporation is preferred due to its ability to channel large amounts of heat into very small volumes. In general, e-beam is preferred over resistively-heated thermal evaporation because crucibles used to hold the evaporant material are water cooled, thus eliminating any film contamination from crucible materials.

4.1.2.2. Thermal Evaporation practice

Once a vapor stream is created, it will condense upon line-of-sight surfaces. This line-of-sight limitation is present to some degree in all PVD techniques, but there are existing engineering solutions that can lessen the severity of the problem. In terms of thermal evaporation techniques, one such method is to introduce a small background pressure of inert gas, such as argon. Argon pressure is raised to a level where the mean-free-path between gas-gas collisions is shorter than the source-to-substrate distance. This ensures that any evaporated atom will undergo collisions prior to condensation upon a substrate. Gas-phase collisions cause oblique scattering of evaporant atoms that result in better coating of off-normal surfaces. While this improves coating uniformity on complex shapes, it negatively impacts deposition rate as a

certain percentage of atoms will be deflected away from the substrate. It should be pointed out that this technique also works for sputter deposition, with the same trade-off between thickness homogeneity and deposition rate.

Electron beam (E-beam) evaporation (commonly referred to in the technical community as E-beam-PVD) is used extensively by the aerospace industry to deposit thermal barrier coatings on turbine blades. It is also extensively used to deposit anti-reflective coatings on lenses and other optical elements.

4.1.3.1. Pulsed Laser Deposition principles

In pulsed laser deposition (PLD), an excimer laser is used to ablate material from a target within a vacuum system which then deposits onto a substrate. By controlling irradiation fluence at the target, deposition rates can be varied from $1\text{-}10^6$ monolayers per second. Alternatively, this can be thought of as a growth rate of up to $100\text{ }\mu\text{m/sec}$. While PLD growth rates are impressive, the primary advantage of PLD is its ability to deposit insulating materials of complex stoichiometry directly from target materials due to its very large instantaneous heating rate. Thermal evaporation of complex oxides is difficult due to limitations imposed by vapor pressures of individual oxide constituents. Sputter deposition of oxides is also difficult due to requirements for special electronic equipment and a very low deposition rate.

4.1.3.2. Pulsed Laser Deposition (PLD) practice

In practice, PLD is complex due to the requirement for coupling laser light into a vacuum system and frequent viewport cleaning procedures necessary to maintain transparency of the optical path between laser and target. There is also a proclivity for massive particle transport rather than simple atomic and cluster transport (i.e., "boulders" being transported along with the "sand"). Finally, as with all PVD techniques, there are line-of-sight limitations. Because of PLD complexities, it is not commonly used for deposition of simple materials, but due to its ease at depositing materials of complex stoichiometry, PLD is routinely used to grow complex oxide materials such as superconducting cuprates.

4.2. CVD

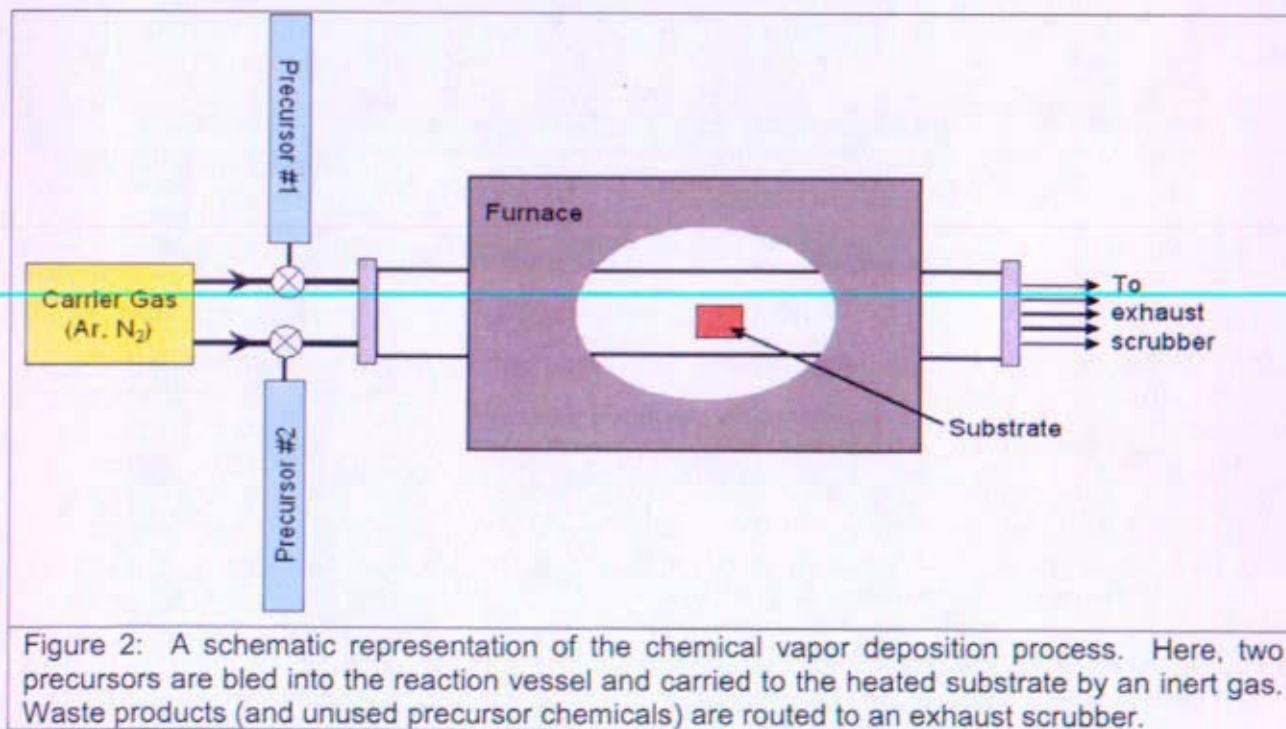
4.2.1.1. Thermal CVD principles

In this coating method, one or more chemical species are flowed through a reaction chamber that is held at elevated temperature and by means of chemical reactions or decomposition, a solid film is grown on a substrate. Table 1 provides examples of some common deposition chemistries, and a schematic of the overall CVD process is shown in Figure 2.

Table 1: A listing of some typical CVD processes, the temperature-range over which they are valid, and the process by-products.[1][3]

W	$\text{WF}_6(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{350-1000\text{ }^\circ\text{C}} \text{W}(\text{s}) + 6\text{HF}(\text{g})$
W	$\text{WCl}_6(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{500-1100\text{ }^\circ\text{C}} \text{W}(\text{s}) + 6\text{HCl}(\text{g})$
Ta	$\text{TaCl}_5(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) \xrightarrow{700-1100\text{ }^\circ\text{C}} \text{Ta}(\text{s}) + 5\text{HCl}(\text{g})$
TiO ₂	$\text{TiCl}_4(\text{g}) + 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{400-1000\text{ }^\circ\text{C}} \text{TiO}_2(\text{s}) + 4\text{HCl}(\text{g})$
TiN	$\text{TiCl}_4(\text{g}) + \text{NH}_3(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) \xrightarrow{575-700\text{ }^\circ\text{C}} \text{TiN}(\text{s}) + 4\text{HCl}(\text{g})$
Al ₂ O ₃	$2\text{Al}(\text{CH}_3)_3(\text{g}) + 3\text{H}_2\text{O}(\text{g}) \xrightarrow{250-500\text{ }^\circ\text{C}} \text{Al}_2\text{O}_3(\text{s}) + 6\text{CH}_4(\text{g})$
Re	$\text{ReF}_6(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{500-900\text{ }^\circ\text{C}} \text{Re}(\text{s}) + 6\text{HF}(\text{g})$
Re	$2\text{ReCl}_5(\text{g}) \xrightarrow{1000-1250\text{ }^\circ\text{C}} 2\text{Re}(\text{s}) + 5\text{Cl}_2(\text{g})$
Re	$\text{Re}_2(\text{CO})_{10}(\text{g}) \xrightarrow{400-600\text{ }^\circ\text{C}} 2\text{Re}(\text{s}) + 10\text{CO}(\text{g})$

The reactions shown in Table 1 demonstrate that, CVD is well suited to compound growth, including oxides, carbides, nitrides, and sulfides. Coating properties and microstructure can be controlled by varying temperature, relative flow rates, and inert gas pressure.



4.2.1.2. Thermal CVD practice

Advantages of CVD over PVD methods include increased conformality of deposits, ability to coat non-line-of-sight surfaces, and ease of compound deposition. However, as CVD is based on chemical reactions, process kinetics and precursor thermal stability typically set an operating

window outside of which films either will not grow, or display deleterious properties. This temperature requirement can cause other difficulties, such as when the required growth temperature is higher than the temperature capability of the substrate. Another drawback to CVD is the need to properly process and dispose of the hazardous gaseous byproducts. As demonstrated in Table I, byproducts from chemistries based on halides are highly active acids (with the initial precursors being extremely hazardous as well). For organometallic chemistries, there are concerns over long-term health effects associated with these chemicals, many of which are suspected carcinogens. These waste products are processed by passing them through a high-temperature oxidation furnace (to fully oxidize organic fragments into H_2O and CO_2) followed by a neutralizing liquid (e.g., NaOH dissolved in water) to neutralize any acidic waste.

CVD is used in a wide variety of applications throughout industry and academia. For example, CVD has been used for a number of years to deposit tungsten for first-level circuit connections in microchips. In some cases, CVD is cost-competitive with powder metallurgy consolidation techniques and therefore free-standing components can be constructed by CVD. Rhenium rocket nozzles are grown in this way by CVD of Re on a molybdenum mandrel rather than a traditional metal-working route. Additionally, CVD and its process variants are the only acceptable way to conformally coat small particles, a process receiving increasing attention from nano-powder producers.

There are a number of CVD variants used within different segments of industry. Pack cementation is one such variant. In pack cementation, a part is placed within a vessel containing a reactive powder (e.g. aluminum or chromium), an inert filler material (such as Al_2O_3), and an activator gas (typically a halide). The container is hermetically sealed, heated to the growth temperature, and then isothermally held throughout the growth process. Activator gas will react with the coating powder forming a volatile compound which transports to the part and releases the metal atom. The driving force for film growth is not a temperature differential, but an activity differential, i.e., the free energy of the metal is lowered by entering into solution with the part. Film thickness is controlled by varying the amount of reactive powder in the container, or limiting the time at temperature [1]. This technique is commonly used to form aluminide films used for oxidation protection.

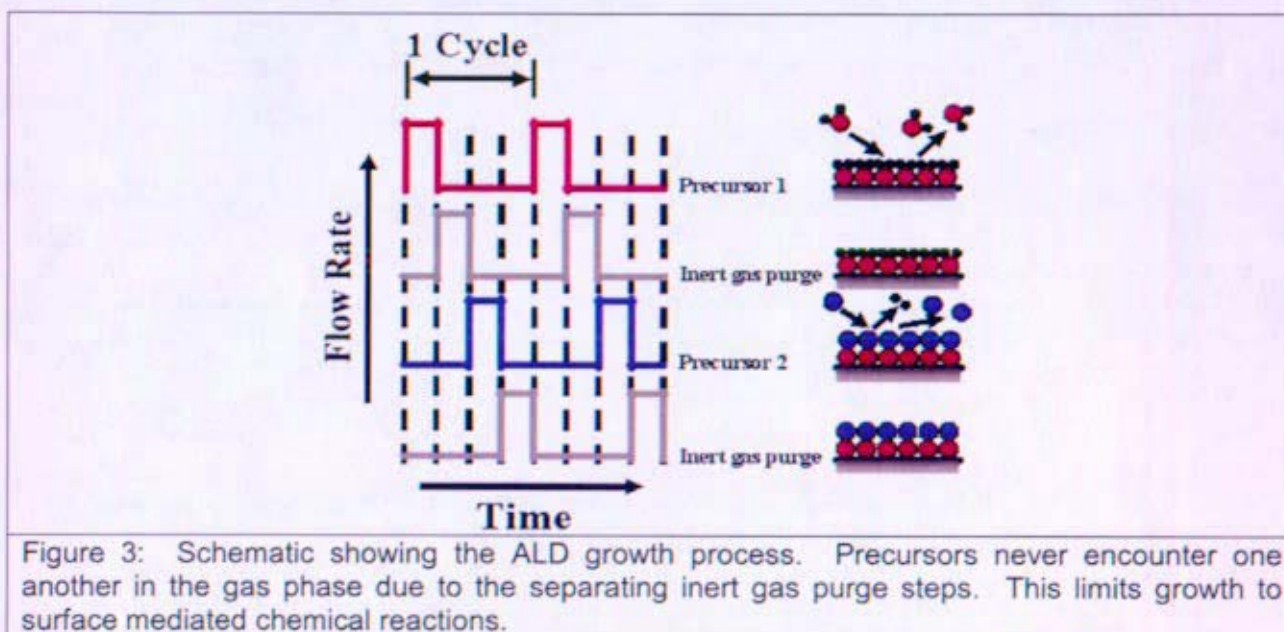
In some cases a substrate may not be able to withstand the deposition temperature necessary to deposit a particular CVD coating. Minimum required deposition temperatures may surpass substrate melting temperatures or lead to undesirable phase transitions within the substrate. For these situations, it may be possible to conduct plasma-enhanced CVD (PECVD). Initiation of a glow discharge (similar to sputter deposition plasmas) within a low pressure CVD process often lowers the temperature required to grow coatings. Plasma injects kinetic energy directly to the precursors via gas-gas collisions and by increasing adatom mobility on growing surfaces. This reduces the heat necessary to sustain CVD growth. Use of PECVD can also increase film growth rates and favor formation of amorphous or very fine polycrystalline films. Drawbacks to PECVD include impurity incorporation due to incomplete byproduct desorption, and in some cases undesirably large compressive film stresses.

4.2.2.1. Atomic Layer CVD principles

Atomic Layer CVD (ALCVD), also commonly called atomic layer deposition (ALD), is a variant of CVD whereby instead of reactant precursors being co-introduced into a reaction vessel simultaneously, they are pulsed into a reaction chamber and temporally separated by an inert gas purge. Gas-phase reactions are eliminated and growth is completely determined by self-

saturative surface reactions. This growth technique requires that precursors cannot react in any way with themselves, i.e., thermal decomposition and multilayer formation are forbidden.

Figure 3 demonstrates a typical ALD process flow. Precursor A is released into a reaction vessel where it forms a single adsorbed monolayer on a substrate. Unutilized precursor A is then flushed out with inert gas, typically N_2 or Ar. Immediately following this purge, precursor B is introduced into the reaction chamber. Selection of B requires that it will react with the exposed molecular groups of A on the growing film surface, release waste byproducts, and leave a single layer of molecular groups that will react with A during the next cycle. A second purging step completes a cycle by flushing out any remaining B molecules. A detailed review of ALD technology is provided in reference [4].



4.2.2.2 Atomic Layer CVD practice

While high temperatures are generally required for CVD, ALD of the same materials typically occur at much lower temperatures. As an example, CVD of Al_2O_3 from trimethylaluminum and water occurs in a temperature range of 250-500 °C[3], whereas ALD from the same chemistry has been reported at temperatures as low as 33 °C.[5] This allows encapsulation of low temperature materials like polymers with hard, chemically resistant coatings. The other primary advantage of ALD is its inherent conformality that is derived from its surface driven reactions. Any surface with an open path to the gas phase can have film grown on it. Studies have shown deposition into structures with aspect ratios of greater than 50:1 with no measurable variation in film thickness.

A practical limitation of ALD is its extremely slow deposition rate. Growth rates are typically on the order of 0.1 $\mu m/hr$, although there are limited reports of catalytic ALD effects resulting in $\sim 1 \mu m/hr$. To become competitive with other deposition techniques, growth rates would have to increase to $\sim 10 \mu m/hr$. Another current deficiency is the limited number of available reaction chemistries. Some CVD processes have readily translated to ALD chemistries, but most do not. Literature surveys provide many examples for ALD of common oxide, nitride, carbide, and sulfide compounds, but relatively few metal chemistries have been reported. Processes have

been established for pure metals within the platinum family (platinum, ruthenium, and iridium) along with tungsten.[6][7][8] New metalorganic precursors are currently under development to provide for elemental deposition of transition elements.[9]

Currently, ALD development is being driven by a need for conformal coatings in microelectronics. With ever shrinking device dimensions in microcircuitry, line-of-sight limitations with sputter deposition prevent coating penetration to the bottom of deep, narrow trenches used for interconnections. As these trench widths continue to shrink, use of sputter deposition results in overly thick films at trench tops that pinch-off in some cases and leave a large void. This compromises the conductivity of the circuit. ALD can eliminate this size limitation. ALD may have applications within the alternator section of the Prometheus reactor. Polymers are considered for use as electrical insulation between wire windings on the stator. To prevent polymer contamination of the He gas, it may be possible to hermetically seal the polymer with an oxide. ALD would allow oxide deposition between closely spaced windings.

4.3.1. Thermal Spray principles

In thermal spray techniques, coating material is supplied to a nozzle in wire or powder form where it is heated and subsequently accelerated to a substrate at high velocity. Upon impact, material is rapidly cooled as it spreads out over the substrate surface. This process can be conducted within a vacuum, inert gas, or atmospheric ambient. While similar to PVD processes, it is generally classed apart from PVD techniques because the coating material is generally not reduced to a vapor. Material is transported in larger, macroscopic particulates. Deposition rates from thermal spray are much more rapid than other PVD techniques, often measured in kg/hr. Thermal spray is useful for depositing metals, ceramics, or a combination thereof. Thermal spray also can generate strong adhesion between typically incompatible materials because of the sound mechanical interactions resulting from impact. Reference [2] provides very detailed information for thermal spray and all of its technical variants.

4.3.2. Thermal Spray practice

There are a number of variations of the thermal spray technique that differ in their method of heating feed materials (see Table 2).

Table 2: Examples of thermal spray techniques and how coating material is supplied in them.

Flame Spray	Feed material is passed through an acetylene torch
Plasma Spray	Two non-consumable electrodes strike an inert gas plasma through which the feedstock must pass
Arc Spray	Two electrodes are made of the feed material and a high current arc is passed between them thereby atomizing the feed
High-Velocity Oxygen Fuel (HVOF)	Variation of flame spray where oxygen flow rates and fuel gas at high pressure generates supersonic flame leads to very high density coatings.

The thermal spray process is popular due to its rapid deposition rate, strong mechanical adhesion between coating and substrate, and ease of use. It is commonly used for deposition

of wear-resistant coatings, environmental barrier coatings, and thermal barrier coatings. There are many experimental parameters that can be used to control properties and structure of the deposit, such as nozzle to substrate distance, substrate heating, and atmospheric content. Drawbacks for this process include oxide inclusions within coatings (only a drawback if one is depositing non-oxides), high-porosity with flame and arc spray processes (5-15%, can be a positive if porosity is desired as in thermal barrier coatings), and line-of-sight limitations. Special guns are available for coating internal sections of pipes and cylinder bores.

5. Review of Protective Coating Literature

5.1. Nb-base Alloys

Protection of Nb-base alloys from high temperature oxidation has been a longstanding objective for metallurgists. Nb suffers from interstitial embrittlement when exposed to a high temperature oxidizing ambient, making protective coatings a necessity. It is common practice for most oxidation protection coatings to use reactive materials that bind with oxygen and form a protective oxide scale. To this end, researchers at General Electric investigated Al-15%Si coatings formed by dip-coating with a follow-on pack cementation procedure. These coatings of 1-10 mils (25-250 μm) were able to limit weight gain in some cases to 0.3 mg/cm²/hr when tested at 1533 K in static air, but the best results were limited to Nb alloys that contained Ti. It was also noted that there was an optimum post-coat annealing temperature of 1313 K. Annealing below this temperature did not impart additional oxidation resistance, perhaps due to a pesting reaction [10].

A program at General Dynamics in the early 1960's studied commercially available protective coatings applied to FS-82 (Nb-32Ta-1Zr). Coatings examined included an Al-10Cr-2Si coating applied by slurry, an Al-50Sn coating applied by slurry, and a Cr-Ti-Si coating applied by pack cementation. All coatings performed well under static heating conditions at 1644 K in 1 atm. of air, with weight gains of <2 mg/cm² after 150 minutes. However, under cyclic conditions (15 min/cycle) there were stark differences. Al-10Cr-2Si coatings began to fail after just 45 minutes, and Al-50Sn coatings displayed twice the weight gain under cyclic conditions compared to static conditions. These failures were presumably due to cyclically driven crack growth. Cr-Ti-Si coatings were largely unaffected by heating conditions and behaved in a similar fashion whether under static or cyclic testing. It should also be noted that at a lower temperature of 1255 K, all three coatings protected FS-82 alloys.[11]

A similar comparative study of industrial coatings was conducted at NASA's Langley Research Center in the same time period.[12] A dozen coatings from nine different vendors were applied to thin (0.5 mm) foils of Nb-10Ti-5Zr and oxidation tested at 1366, 1588, and 1755 K. Coatings based on borides and aluminides did not perform well at any temperature; NbB₂ coatings failed within a few hours of the initiation of testing while the NbAl₃ coating failed within 40 hours at the lowest testing temperature and failed within minutes at the highest. Silicide coatings provided superior protection that increased with addition of titanium or chromium, with the best protection provided when both were added. At 1366K, Cr and Ti containing silicides survived more than 220 hours of static oxidation testing. Within this group of coatings, films grown by pack-cementation outperformed those deposited by vapor phase techniques.

The mechanism by which silicides provide high temperature oxidation protection to Nb alloys is through the formation of a protective, amorphous silica layer on the exposed surface. Simple Nb silicides suffer from low temperature oxidation problems referred to as "pesting", whereby a rapid and non-protective oxidation process occurs that can completely destroy the material.

Therefore, complex silicides have been developed for Nb protection such as Si-20 wt.% Fe-20 wt.% Cr (R512E). The R512E coating was optimized for Nb alloys Cb-752 (Nb-10W-2.5Zr) and D-43 (Nb-10W-1Zr-0.1C), but tests on other Nb alloys such as FS-85 (Nb-10W-28Ta-1Zr) and C129Y (Nb-10W-10Hf-0.1Y) show the coating to protect very well across the Nb-alloy family. Cyclic oxidation tests with 40 minute cycle times over temperature profiles similar to what would be expected during atmospheric re-entry of a spacecraft (673-1573 K) demonstrated the R512E coating to withstand over 200 cycles without failure. If tested under lower pressures (<35 Torr), a higher Cr content (Si-40Cr-20Fe) resulted in slightly higher cycles to failure. Different formulations containing Mo, W, Ti, and V offered no additional protection, and in most cases reduced protection.[13]

Other cyclic oxidation tests at 1573 K with R512E coated Nb and Nb-alloys demonstrated lifetimes between 89-155 hours, with alloys containing strong oxide formers (Ti, Hf, Zr) tending to have longer lifetimes in proportion to levels of alloying. This is contrary to the above data indicating no additional advantage from adding titanium. Presumably the group IV elements act as oxygen scavengers when located within Nb-base alloys, inhibiting the onset of interstitial embrittlement, but when included within silicide coatings they interfere with the formation of protective silica. Microscopic and spectroscopic measurements revealed formation of a multilayer coating of various complex silicides, but no diffraction-based structural measurements were made.[14] Simple Nb-silicides remain unacceptable, as recent work with boron additions to simple Nb₅Si₃ demonstrate. Even though B additions enhance the growth of a glassy borosilicate layer, there is concurrent, competitive formation of Nb₂O₅ which prevents the formation of a passivating layer.[15]

NASA and the Army carried out a joint project to study modifications to the R512E coating system. Mn additions, or the outright replacement of Fe with Mn, were observed to result in 100% improvements in performance during oxidation in slow-cycle ambient pressure tests up to 1643 K. Attempts to alter the crack frequency within the coating by the addition of modifiers (W, Al₂O₃, and ZrO₂-CaO) had some success at improving life (25% with Al₂O₃ and 20% with ZrO₂-CaO), but no universal relationship between crack frequency and coating life was measured.[16]

5.2. Ta-base Alloys

Because Ta belongs to the same chemical group as Nb, it suffers from the same interstitial embrittlement problem and needs to be protected from oxygen and carbon at high temperatures. Hallowell *et al.*[17] studied formation of silicides for oxidation protection on Ta-10W, T-111, and Ta-30Nb-7.5V. Silicides were formed by pack cementation, typically to a thickness of 4-8 mils (100-200 μ m) and tested with a mix of static and cyclic-oxidation. Inclusion of vanadium or boron into the pack during coating resulted in significantly increased oxidation life (to greater than 100 hours in the case of cyclic oxidation at 1528 K). This was attributed to vitrification of the surface silica scale that formed during testing. However, while the addition of V and B increased oxidation protection, they also caused severe embrittlement of the Ta-alloy. For boron, this was traced to formation of an intermetallic phase at grain boundaries. For vanadium, it was suggested that calcium impurities in the initial V source caused the embrittlement.

Another oxidation protection scheme made use of a low temperature eutectic of Sn-Al.[18] Testing data were sparse, but it was noted that a Ta-10W sample survived 3 hours at 2200 K with a 1-2 mil (25-50 μ m) coating of the Sn-Al compound. This coating was also self-healing, presumably due to a molten Sn-Al mixture underneath the surface oxide layer that forms during

testing. This protective coating would not be appropriate for a high gas flow-rate system as it would not be likely to withstand the shear forces from the gas.

Use of a pure tungsten silicide coating, where W was deposited by CVD and then silicided by pack cementation, resulted in logarithmic oxidation rates in a temperature range of 1273-1773 K (oxidation rate decreasing with increasing temperature in this range). At 1973 K, oxidation rates were extremely rapid (almost exponential) and did not result in growth of a protective silica layer. Use of a 95W-5Ti slurry coat, followed by a sintering step and then subsequent siliciding by pack cementation resulted in a coating that demonstrated a parabolic oxide growth rate at all of the testing temperatures. Oxidation protection of Ta-10W for up to one hour at 1973 K was demonstrated with this Ti modified WSi₂. For both unmodified and Ti-modified silicides, coatings survived the entire test duration of 60 minutes at 1773 K and below.[19]

As with Nb, silicide coatings on Ta also suffer from pesting phenomena in intermediate temperature ranges. Falco and Levy studied the oxidation protection of a (50W-20Mo-15V-15Ti)Si₂ coating sprayed on Ta-10W [20]. Based on a systematic thermogravimetric analysis, pesting was found to occur at temperatures between 1033 and 1144 K. Between 1200 and 1311 K, modified disilicide coatings offered complete protection up to 200 hours (weight gain saturating at 2.2 mg/cm² after 3.5 hours). Most importantly, it was found that a pre-oxidation treatment at 1311 K for 330 minutes eliminated coating failure during subsequent oxidation testing within the pesting temperature range. Further work showed pesting could also be avoided by heating past the pesting temperature range at a rate ≥ 6 °C/min. It was also observed that this silicide composition was self-healing, due to disappearance of cracks with prolonged testing. Also, testing under a nitrogen atmosphere eliminated crack formation in the coating, indicating that crack formation during testing is an oxidation related phenomenon.[21]

Self-healing of cracks in silicide coatings is highly desirable, because a common failure mechanism of these films is through crack formation and enlargement due to thermal stresses during cyclic-oxidation. To promote self-healing in silicides on Ta, Packer and Perkins attempted to develop coatings with a goal of controlling viscosity and plasticity in the resultant oxides.[22] If successful, oxides could then flow into fissures and provide for the necessary self-healing. To this end, oxide systems were identified that form eutectics with silica and could potentially provide this desired fluxing effect. After cyclic oxidation tests at 1700 K and 10 Torr of air pressure (15 minute heat-up, 30 minute hold, 15 minute cooldown), four systems demonstrated lifetimes greater than 100 cycles: 20Mn-27Ti-53Si, 25Zr-30Mn-45Si, 24Ti-24Co-52Si, and 33Co-22Mo-45Si. CoTiSi and MoCoSi were abandoned due to inconsistent results and MnZrSi was not pursued further because the oxide that developed was very fluid and evidence of massive flow was observed following testing. However, all of the oxide systems may be feasible if operating temperatures are significantly reduced.

Another finding of Packer's study was the importance of oxygen pressure and annealing temperature on oxide stability. There is a transition pressure above which silicides will form a passivating oxide and below which they will actively oxidize, resulting in rapid failure (failure of coating followed by substrate failure). This transition pressure increases with increasing temperature. For example, with the MnTiSi coating, the transition pressure was found to be between 0.1 and 1 Torr at a temperature of 1700 K and between 1 and 10 Torr when the temperature was 1811 K.[22]

5.3. Mo-base Alloys

As with Ta and Nb, work on protective coatings for Mo has largely focused on silicides. MoSi₂ coatings on Mo-0.5Ti were tested at 1644 K under both continuous and cyclical heating conditions in air.[23] Protection was obtained through formation of a glassy silica phase on the exposed disilicide surface. Failure occurred after silica underwent a phase change to cristobalite and the concurrent change in density formed craze cracking at the surface. Failure was exacerbated by thermal cycling which served to repeatedly open and close cracks, exposing fresh surface area to the oxidizing ambient during each cycle. Boron additions to MoSi₂ resulted in oxidation protection for longer times, presumably through inhibition of the nucleation of cristobalite and stabilization of a glassy phase.

MoSi₂ is also subject to a pesting reaction at low temperatures. Below 1073 K, oxidation of MoSi₂ produces MoO₃ in competition with SiO₂. Volatile MoO₃ prevents formation of a protective SiO₂ layer and the silicide typically disintegrates. Above 1073 K, oxidation of MoSi₂ results in the formation of a protective SiO₂ layer at the surface and Mo₅Si₃ between the SiO₂ and MoSi₂. While Mo and its dilute alloys have been protected by MoSi₂, Mo-Re does not benefit from this silicide coating. Pack cementation deposition of MoSi₂ on both Mo-41Re and Mo-49Re resulted in virtually no protection of the underlying alloys; significant weight loss was observed in a majority of samples heated to 1533 K in one atmosphere of air. Conversely, 25 µm of R512E offered protection for ~90 hours before onset of catastrophic weight loss.[24]

Use of platinum has been investigated for high temperature protection against oxidation and subsequent volatilization of Mo. However, Mo readily diffuses through Pt, oxidizing at the surface and volatilizing as well as forming brittle interfacial intermetallics (Pt₂Mo and PtMo). There are also experimental data showing localized debonding between Pt coatings and Mo substrates, perhaps due to oxygen diffusion through Pt.[25] Research has been conducted on diffusion barriers to limit or eliminate this Pt/Mo interaction. TiB₂, TiN, TiC, and TaC were examined and all were found to metallurgically react with Pt and/or Mo to varying degrees. This makes it unlikely that any of these barriers would be worth further pursuit, especially for the long times necessary for Prometheus.[26]

A major concern with using a silicide on Mo (as well as other refractory metal alloys) is gradual loss of Si into Mo over time at high temperatures. This diffusion of Si leads to formation of less protective silicides (Mo₅Si₃), and incorporation of Si into the bulk Mo-alloy can compromise mechanical properties. Recent work for protecting Mo has studied amorphous barrier layers based on the Mo-Si-C-N quaternary system, placed between Mo and MoSi₂. [27] The authors claim that diffusion of carbon into Mo from this film is minimal. However, Auger scans in the same study indicate that absorbed carbon could be as high as 10 at.%. This high C uptake would be absolutely unacceptable for the more active refractory metals (Ta and Nb).

5.4. General Coatings for Refractory Metal Alloys

Rather than using oxide formers such as aluminides or silicides, another possibility for high temperature protection is the use of another refractory metal as a blocking layer. In the SP-100 program, Nb-1%Zr was selected as fuel cladding material, but it is incompatible with UN fuel and some fission products, hence a barrier material was required. Tungsten was originally chosen, but was later abandoned due to its brittleness and was replaced by rhenium. In this particular case, rhenium was formed into a tube, placed inside a pre-existing Nb-1%Zr tube, brazed, and then HIPed to form a bonded structure.[28]

Rhenium has been used extensively for liquid rocket engine thrust chambers as a replacement for R512E coated Nb-alloys. The limiting factor for high temperature use of Re is its formation of volatile oxides at temperatures above 633 K.[25] To protect Re, iridium was chosen because it is oxidation resistant at 1273 K, has a high melting point (2719 K), and has a coefficient of thermal expansion (CTE) similar to Re ($6.4 \times 10^{-6} \text{ K}^{-1}$ and $6.2 \times 10^{-6} \text{ K}^{-1}$ for Re and Ir, respectively).[29] These duplex coatings are grown sequentially by CVD on a molybdenum mandrel which is subsequently removed chemically, leaving a free-standing part.[30] Typically, the Ir coating is 50-100 μm thick with a base rhenium thickness of 2500 μm .

The entire platinum metals group (Pt, Pd, Ir, Rh, Os, Ru) has been evaluated for protection of refractory metal alloys because of the general oxidation resistance the Pt group demonstrates. Ir has been the focus of these efforts because it shows the highest minimum melting temperature with each refractory metal, has perhaps the lowest permeability for oxygen, and has smaller interdiffusion coefficients with refractory metal alloys as compared to other Pt group members.[31] Iridium has excellent resistance to oxidation; it forms a stable, stoichiometric IrO_2 at 1373 K and below. At higher temperatures, mass loss occurs linearly with time due to formation of volatile IrO_2 and IrO_3 . For example, at 7.5 Torr (air) and 1950 K, recession rates are $\sim 2 \text{ \AA/sec}$. This rate can be decreased by 25% if iridium is alloyed with aluminum to form an aluminide.[32] Vapor pressure of metallic Ir is very low, only 0.065 Torr at its melting point.[33]

Limited solubility for carbon in both metals is another positive aspect for Ir/Re bi-layers. As Ta and Nb alloys are severely embrittled by interstitial carbon, it is important to prevent any gaseous, carbon containing species from reaching them. In the temperature range of 1093-1529 K, solubility of C in Re ranges from 0.085 to 1.67 at.%, respectively. For iridium this solubility range is 0.033 to 0.25 at.%. [34] These limited carbon solubilities combined with the lack of a carbide phase for either metal suggest that Ir and Re will not act as a sink for carbon, unlike Ta or Nb which both have significant affinity for carbon and form carbides. However, this does not preclude a potential for rapid carbon diffusion through these metals, particularly along grain boundaries and defects. Diffusion data for carbon in these metals are not readily available.

There is significant solubility in both terminal solid solutions within the Re-Ir system (28 at.% in Ir and 38 at.% in Re). Significant mutual solubility increases concerns over coating failure from Re diffusion through Ir to the exposed surface.[35] The limited information available on the interdiffusion of Re and Ir suggests that Re diffuses into Ir coatings primarily along grain boundaries. However, in his review of Ir/Re, Ohriner notes that "[the Ir] coating life has substantially exceeded that predicted by this diffusion-related failure mechanism".[32] Test results show that Ir/Re is capable of withstanding 3600 rocket firing tests at a temperature between 2200-2477 K, with a cumulative burn time of 12 hours. After this testing there was no measurable internal erosion of the Ir/Re chamber.[36] While primarily used as standalone parts, Ir/Re bilayer coatings have also been grown on Ta-10W. Ir provides oxidation resistance and Re serves as a diffusion barrier between Ir and the Ta alloy.[37] While coating development on Ta-10W was demonstrated, there were no accompanying thermal or microstructural data.

5.5. Ni-base Superalloys

Development of the Ni-base superalloys has primarily focused on their high-temperature (900-1350 K, for short times at the highest temperatures) mechanical properties. Oxidation resistant Ni-base superalloys contain at least 18 wt.% Cr to form an external passivating oxide film of Cr_2O_3 . However, use of these alloys in extremely aggressive environments such as those encountered within a jet engine, requires a level of corrosion resistance that the base alloys do

not possess. By the early 1960s it was evident that use of these alloys in jet engines for times spanning tens of thousands of hours would require additional protective coatings.

Initial research focused upon Cr-base coatings, because Cr provides oxidation resistance in the base alloys. Cr was soon abandoned in favor of Al due to formation of a weak interface and the superior oxidation resistance of Al above 1090 K. Also, chromide and silicide coatings are limited to below 1223 K as they form volatile, unprotective oxide/hydroxide species [38]. This may be due to reaction with high-temperature water vapor, see section 5.6 for the case of Si-hydroxide. Al reacts with Ni-base alloys to form Ni-aluminides, with β -NiAl as the most desirable. Aluminides with higher Al content have lower melting points which lessens their attractiveness, whereas those phases with higher Ni content have reduced oxidation resistance as compared to NiAl. Additions of Ta to Ni-Al raise the coating melting point and can enhance diffusional stability with respect to the substrate.[39]

Protection from aluminide coatings is provided by formation of an Al_2O_3 layer on the exposed surface. Alumina will protect the underlying aluminide coating as long it does not erode or spall off. As spallation occurs (either from high-gas flow erosion or due to thermal-cycling induced stress), Al_2O_3 will reform on the surface (self-healing) and deplete Al from the coating "reservoir". As this process continues and Al is further depleted with time, oxides richer in Ni will begin to form (spinel NiAl_2O_4 , and NiO). Mass transport is greater through these phases than through pure Al_2O_3 , thereby increasing overall oxidation rates. Above ~ 1270 K, diffusion of Al into the superalloy will also decrease the availability of Al for oxidation.[39]

To further improve durability and efficacy of aluminide coatings, a variety of dopant materials have been investigated. Chromium additions are observed to improve adherence of oxide scales[40], yttrium and cerium improve scale adherence and slow overall oxidation rates[41], and platinum additions, while not playing a direct role in oxidation, increase the activity of aluminum and improve hot corrosion resistance (resistance to sulfur and salt corrosion at high temperatures).[42] Investigation of these additions have led to the M-Cr-Al-X coating system (where M=Ni, Co, and/or Fe, and X= active element addition(s) such as Y, Si, Ta, Hf), an example of which can be seen in Figure 4. The primary advantage of Cr is that it lowers the amount of Al required to form and maintain Al_2O_3 from 10% to 5%. It is desirable to limit the concentration of Al because it decreases coating ductility. Reactive element additions provide enhanced scale adhesion and decreased oxidation kinetics, as stated above.[43][44][45][46]

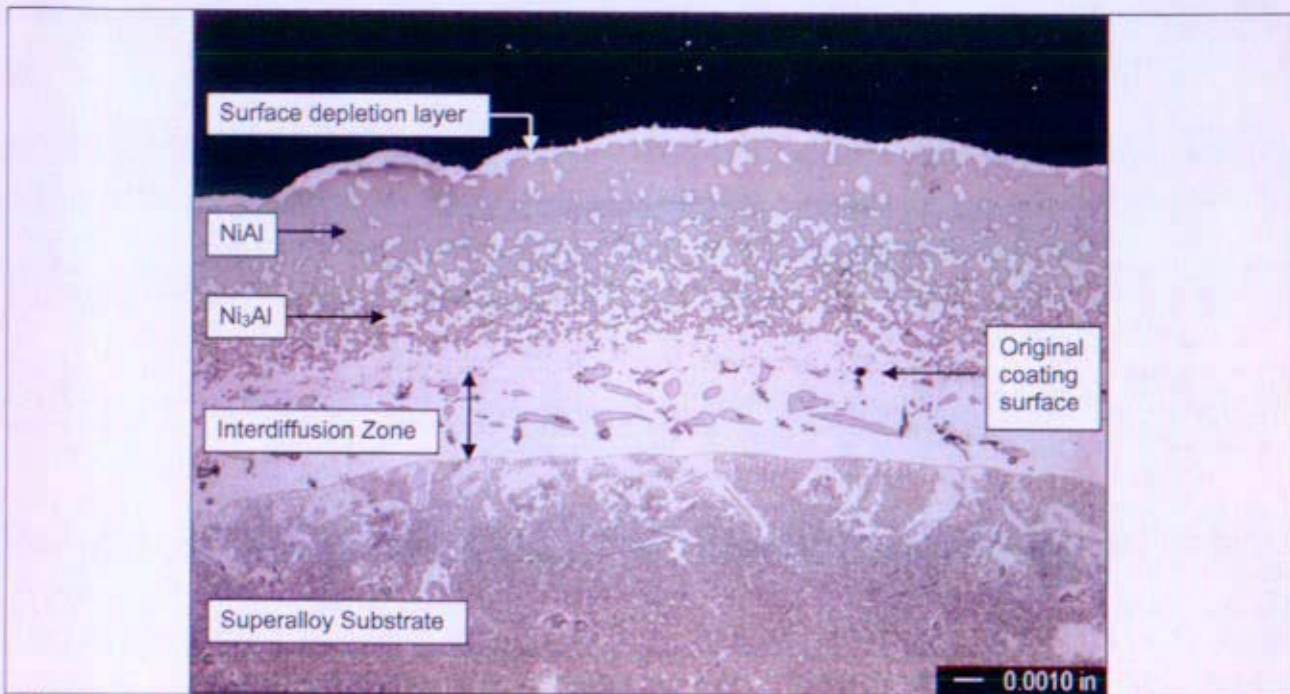


Figure 4: An example NiCrAlY coating on a Ni-based superalloy, taken from a turbine after significant usage. Formation of the Ni-rich aluminide phase is well along, and the interdiffusion zone between coating and alloy substrate is over 50 microns thick. Note: protective oxide surface scale is not visible at this magnification. [42]

While use of reactive elements increase scale adhesion, several investigators found that the amount of residual sulfur in superalloys also strongly affects the oxide scale adhesion. Excellent scale adhesion is observed for sulfur values at or below ~ 0.2 wppm. A number of authors have proposed that prevention of sulfur segregation to grain boundaries by chemically binding to reactive element additions (such as Y) is the reason these additions improve oxide scale adhesion.[45][44]

Diffusion aluminide and MCrAlY coatings are highly mature technologies based on over fifty years of research and volumes of data that are available in open literature sources. Current research focuses on development of diffusion barriers between aluminide coatings and superalloy substrates to inhibit Al depletion from the coating [47], trying to understand mechanisms behind alloying effects [48], and attempts to further control scale formation and growth rate in order to improve adhesion of thermal barrier coatings on top of these Al based EBCs.[46]

5.6. SiC

Environmental protection for refractory metal alloys is required to prevent interstitial embrittlement and mass-loss due to reactions with oxygen and carbon at high temperatures. For SiC, the issue is one of ceramic volatility. SiC has been identified for use in next generation gas turbines operating at very high temperatures ($T > 1700\text{K}$). Like most Si containing materials, SiC will form a thin, protective surface layer of SiO_2 that prevents rapid oxidation and subsequent degradation. In gas turbine environments, there is also the presence of reactive alkali metal compounds and water vapor that destroy this protective silica film. For instance, Na_2SO_4 , (as a fuel contaminant or from marine environments) dissolves silica by forming a liquid silicate phase that is easily eroded. In the case of water, a gaseous hydroxide, $\text{Si}(\text{OH})_4$, is formed. This volatile hydroxide continuously removes protective silica and leads to recession of

the SiC component.[49] As a result, EBCs developed for SiC have been designed to limit this recession and isolate SiC from environmental interactions.

High-temperature oxides have been the focus of SiC EBC research. Plasma-sprayed mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is used for SiC protection because of its chemical compatibility and similar CTE. A limitation of plasma-sprayed mullite is its tendency to crack and debond from SiC when thermally cycled above 1223-1273 K due to crystallization of amorphous regions present in as-sprayed mullite coatings. This was partially alleviated by conducting plasma spray depositions above the crystallization temperature, in order to deposit a fully crystallized coating. The result is a reduction of SiC oxidation kinetics by a factor of 2-3 at 1573 K under 20 hour cycles. However, for 1 hour cycles at 1573 K and 1673 K, oxidation was actually accelerated, presumably due to larger thermal strains.[50] This indicates that while the thermodynamics and/or kinetics of a reaction may be favorable, other factors in the engineering application (e.g., stresses and strains) may remove that advantage.

A limitation of plasma-sprayed mullite is its porous microstructure. Porosity can be eliminated in mullite through CVD growth. Mullite grown on SiC fiber (Nicalon) by CVD has been accomplished using AlCl_3 and SiCl_4 precursors. Static oxidation testing (1000 standard cubic centimeters per minute (sccm) of O_2 at 1573 K) of this coated Nicalon fiber for 200 hours resulted in less than 1% weight gain, whereas uncoated fiber increased in weight by greater than 14%. Under cyclic oxidation conditions (250 sccm O_2 , 1 hour to heat to 1273 K, 1 hour to cool), weight gain of coated Nicalon fiber was ~1% after 250 cycles.[51] CVD of mullite has not yet been embraced by industry as it cannot compete with fast deposition rates inherent with plasma spray processes.

The addition of an yttria-stabilized-zirconia (YSZ) top-coat over mullite significantly reduces water-mediated volatile loss of silica, as well as total mass gain due to cyclic oxidation at 1573 K for up to 100 hours.[49] Also, flexural test results indicate that mullite/YSZ duplex coatings help maintain the mechanical properties of SiC in humid environments at 1589 K.[52] However, beyond 100 hours mullite/YSZ coatings develop an enhanced oxidation rate due to water penetration through cracks. YSZ, while selected for its resistance to attack by water vapor, suffers from a large CTE mismatch with mullite and SiC, and therefore promotes crack nucleation and growth.

Even with a fully crystallized mullite coating, film through-cracks remain the weak link as they provide fast diffusion paths for water to attack SiC. An improved top coat for mullite has been developed from $\text{BaO-SrO-Al}_2\text{O}_3\text{-SiO}_2$ (BSAS) with substantially improved crack resistance. Further durability is provided by insertion of a Si bondcoat layer between mullite and SiC. A cross-sectional SEM image of this BSAS/mullite/Si/SiC system is shown in Figure 5. Durability of this coating configuration has been demonstrated for up to 1000 hours in 2-hour cycling at 1573 K in 90% $\text{H}_2\text{O/O}_2$. [53]

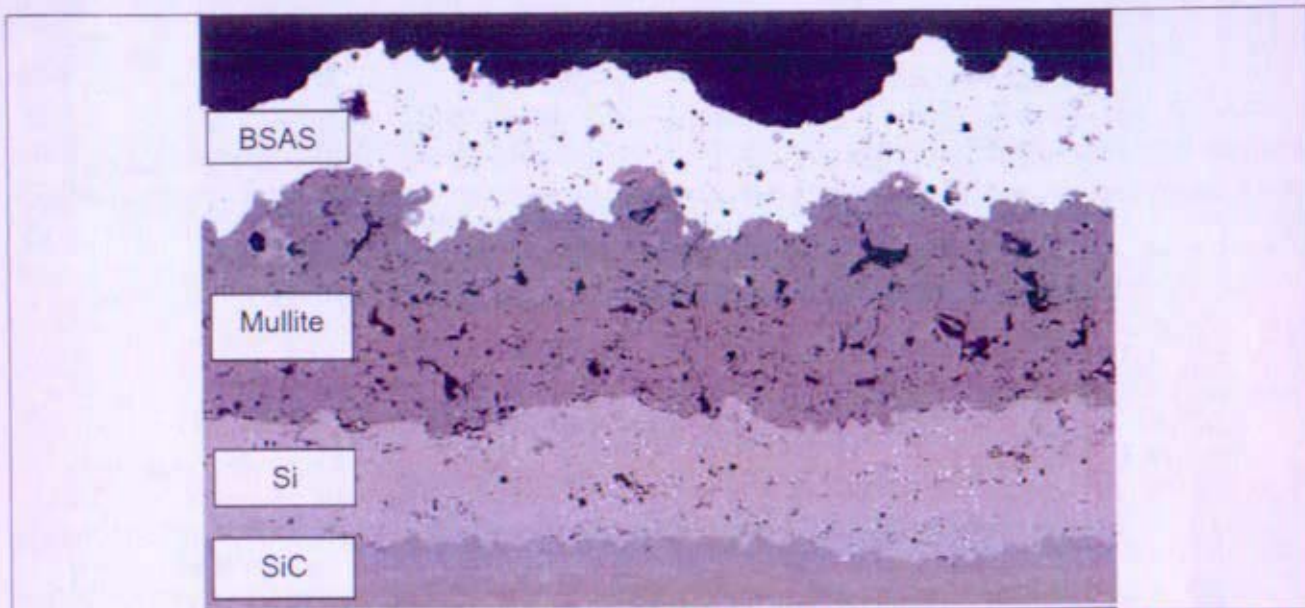


Figure 5. A cross-sectional SEM image of a BSAS/Mullite/Si EBC coating on SiC. The coating was applied by air plasma spraying. [54]

Plasma-sprayed BSAS/mullite/Si/SiC (similar to Figure 5) and BSAS/BSAS-mullite/Si/SiC systems have been tested on combustor liners for times up to 14,000 hours. Both offer significant protection, but the configuration with a mixed BSAS-mullite layer better prevents oxygen penetration to the Si layer. Because this coating system is complex and comprised of multiple sublayers, there are multiple failure modes. The primary mode comprises volatilization and erosion of the BSAS layer during use which leaves mullite exposed to attack. Exposed mullite will then separate into SiO_2 and Al_2O_3 and the silica will volatilize as the hydroxide species leaving a porous, non-protective alumina layer behind. In a different mode of failure, pre-existing flaws in BSAS and mullite layers lead to rapid oxidation of the Si bond coat and subsequent spallation at the newly formed SiO_2 /mullite interface. These pre-existing flaws can arise during coating deposition or from tool bumps (i.e., pre-existing damage sites). [54]

5.7. Summary and Applicability to the Prometheus Reactor

Oxide-based Refractory Metal Alloy Protection:

The primary focus for environmental protection of refractory metal alloys has been the various silicides. The advantage of these coatings lies in their ability to form a protective, slow growing silica layer when exposed to high temperature, oxidizing conditions. Disilicides (MSi_2) have received the greatest attention, due to their increased silicon activity as compared to the lower silicides (M_5Si_3). Silicide research has been favored over aluminide because at the high temperatures of interest, SiO_2 has an elastic modulus a factor of five smaller than Al_2O_3 and is therefore better suited to handle shock and strain from thermal excursions. Another key factor is rapid diffusion of Al into Nb and Ta. [55] Other oxide formers have been evaluated and rejected for various reasons: Ti, Zr, and Hf are all strong oxide formers, but they are non-stoichiometric at elevated temperatures and display very rapid oxygen diffusion rates making them unsuitable for oxidation protection coatings. Beryllides also strongly form oxides, but Be diffusivity in refractory metals is faster than Al and as Be is smaller than O and C, it would likely lead to interstitial embrittlement of Ta and Nb alloys. While silicides suffer from mid-temperature

pesteing difficulties, this is easily addressed through pre-oxidization at high temperature prior to service entry.

Of primary concern are the atmospheric differences between proposed Prometheus reactor designs and that for which silicide coatings were originally designed. Previous applications for which silicide coatings were chosen all had one thing in common: the expectation that refractory metal alloys need to be protected at high temperature (1200-1400 K) from atmospheric pressure air, be it for a re-entry heat shield, rocket nozzle, or gas turbine engine. Silicides require an oxidizing atmosphere to form protective silica and the proposed Prometheus environment will contain very low levels of oxidizers. Even if silica were to be formed prior to its entry into service by a pre-oxidizing step, there still remains a minimum level of oxidizing gas required to maintain oxide stability and prevent decomposition of silica into a volatile oxide gas.

A thermodynamic analysis illustrates the inherent instability of silica under weakly oxidizing or inert conditions (all thermochemical data used for volatility calculations were obtained from [61]). Figures 6 (a) and (b) are volatility diagrams for the Si-O system at 900 and 1420 K, respectively (this is the temperature range that has been provisionally attached to the fuel pin cladding in the Prometheus reactor [56]). These diagrams provide equilibrium vapor pressure of gaseous species with respect to solid phases (here, Si and SiO₂). The equilibrium equations upon which these diagrams are based are a function of oxidizing pressure, but data are presented here in terms of $\log[P(\text{H}_2\text{O})/P(\text{H}_2)]$ rather than $\log[P(\text{O}_2)]$ because water vapor impurities are typically the oxidizing species available in high temperature gas reactors (HTGRs). For reference, graphite-core high-temperature gas reactors (GC-HTGRs) [57] typically operate in a $[\text{H}_2\text{O}]/[\text{H}_2]$ range of ~ 0.0044 ($\log(0.0044) = -2.4$), denoted by orange boxes in Figure 6. With this level of water vapor at 900 K, SiO₂ is highly stable, because the equilibrium partial pressure of the dominant gaseous specie, SiO, is only $\sim 10^{-19}$ atm ($\sim 8 \times 10^{-17}$ Torr). It should be noted that in the absence of a graphite core the impurity ratios will likely be very different, but the HTGR literature provides a preliminary frame of reference upon which to base discussion.

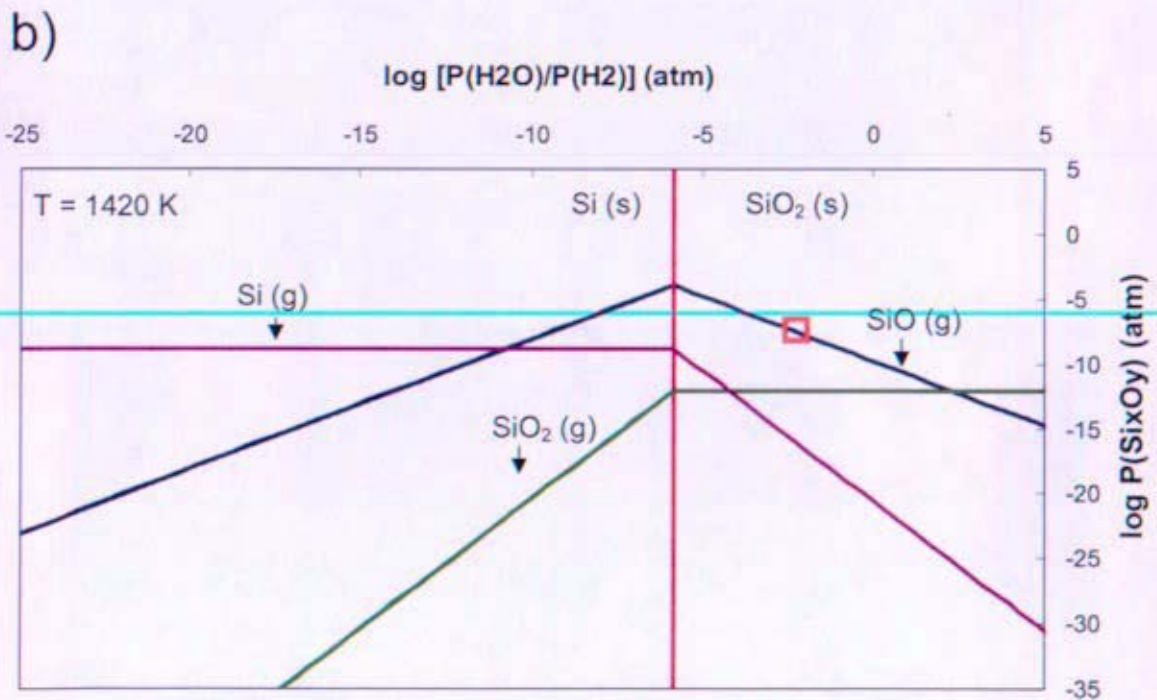
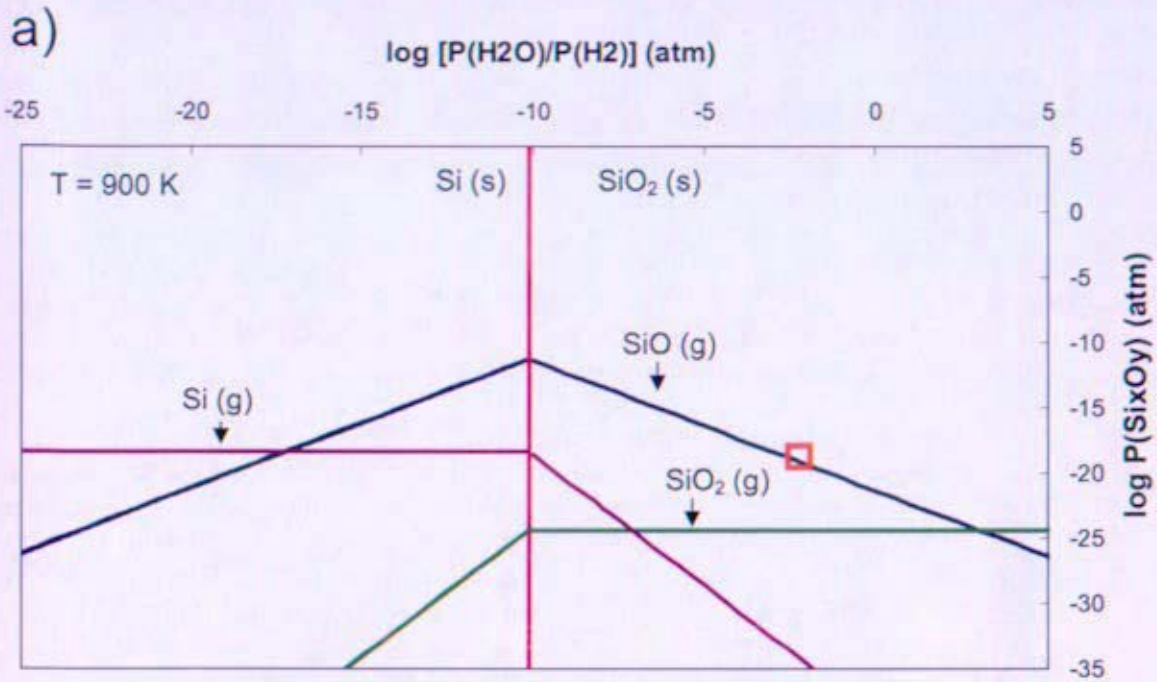


Figure 6. Si-O volatile species at a) 900 K, and b) 1420 K. Orange boxes represent the typical $[\text{H}_2\text{O}]/[\text{H}_2]$ fraction measured in HTGRs.

A recession rate can be calculated from these equilibrium pressures using kinetic gas theory. Impingement rate of a gas on a surface is given by:

$$I = \frac{P}{(2\pi mkT)^{1/2}} \left(\frac{\text{molecules}}{\text{cm}^2 \text{ sec}} \right)$$

where P is gas pressure, m is the molecular weight of the gas molecule, k is Boltzman's constant, and T is absolute temperature. Growth (or erosion) of a surface is given by altering the P term to $P - P_0$ where P is the pressure of the impinging of gas that contributes to growth, and P_0 is the equilibrium vapor pressure of the surface material. If the situation is such that any material that escapes from the solid surface is removed from the system (i.e. pumped away), the above formula divided by atomic density of the solid yields the material recession rate. Use of this formula for the 900 K case given above yields a recession rate of $\sim 10^{-19}$ m/min, i.e., there is no recession and SiO_2 will be stable.

At 1420 K, the situation is very different (see Figure 6b), with an equilibrium SiO vapor pressure of $\sim 10^{-8}$ atm ($\sim 2 \times 10^{-5}$ Torr), or an increase of 10^{11} over that at 900 K. The result is a recession rate of $\sim 10^{-7}$ m/min, a non-trivial value. Summed over the planned reactor lifetime (120,000 hours), this yields a total recession of about 60 cm. It should be noted that these calculations are based on a few assumptions, namely they neglect any oxidizing contribution from CO, and the presence of 13.6 atmospheres of He/Xe overpressure. Figure 7a is a semilog plot that demonstrates the temperature dependence of estimated recession rate. Values are deceptively small in Figure 7a, for example, ~ 0.001 Å/min at temperatures around 1100 K, but when multiplied by the total mission life the total recession becomes a troubling figure of ~ 1 μm (see Figure 7b). It should also be pointed out that this is merely assuming a steady-state case; thermal excursions as small as +50 K can increase recession rates by an order of magnitude.

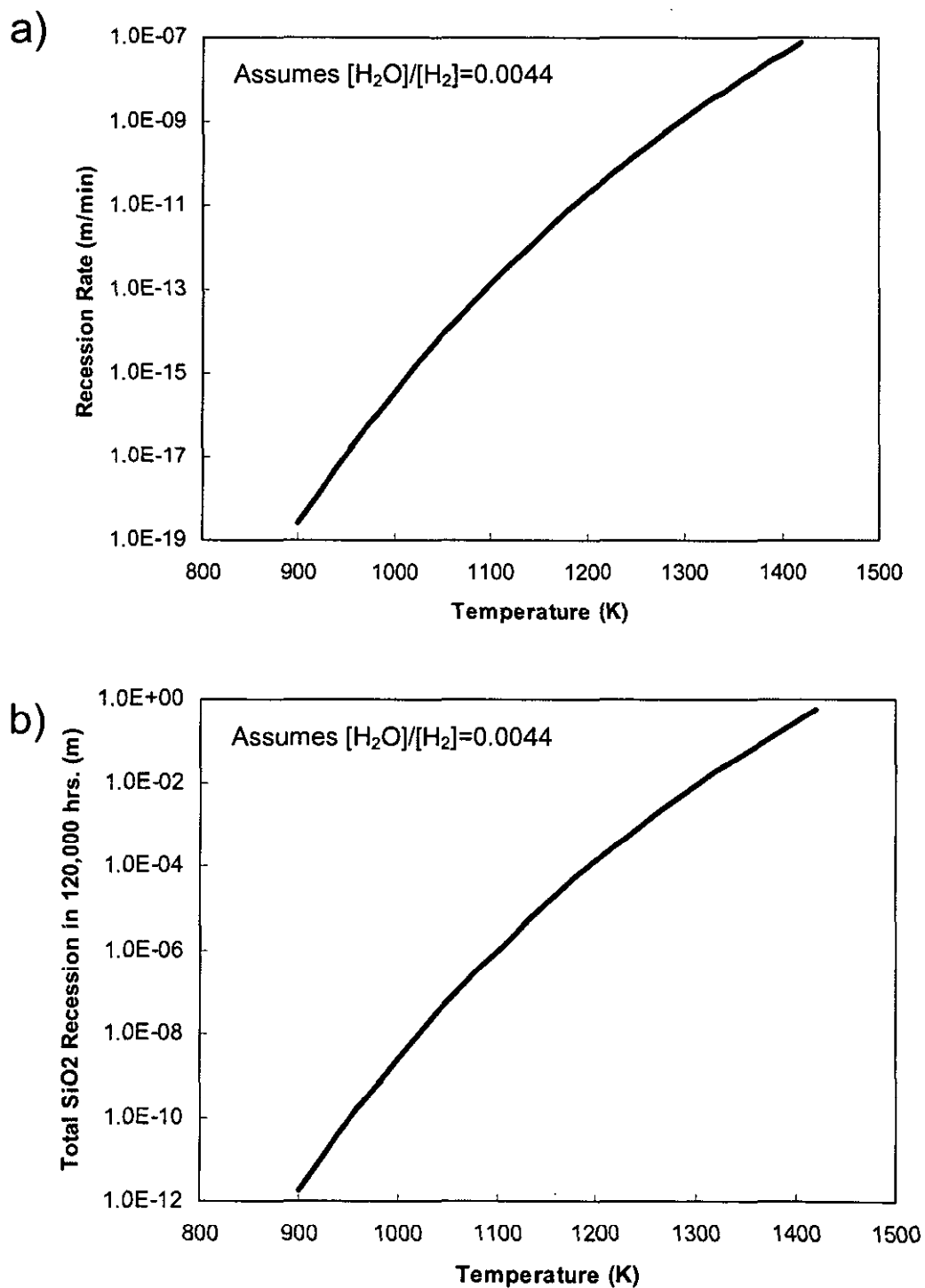
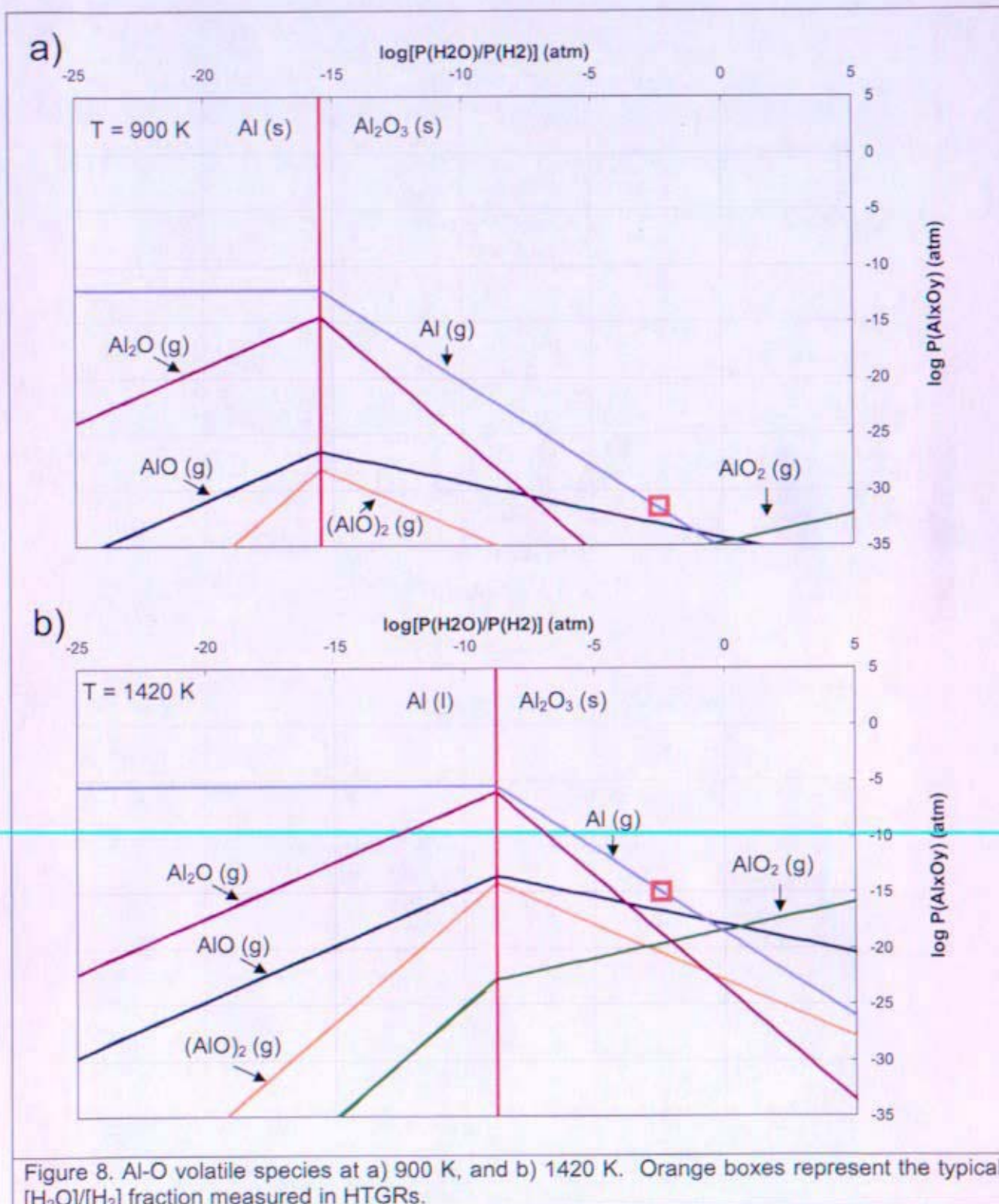


Figure 7. a) Estimated effect of temperature on recession rate for silica, assuming a $[H_2O]/[H_2]$ fraction of 0.0044, and b) total silica recession in 120,000 hrs. Recession expected with SiO₂-former coating for Prometheus applications would be unacceptable at the proposed high temperatures.

Loss in chemical stability of silica at high temperature is clearly depicted in Figure 7. To qualify a silicide for use above 1100 K, silica must be included in materials compatibility modeling efforts to more accurately quantify silica volatilization, and to determine the effects volatile SiO could have in colder portions of the gas circulation loop. Also, use of a silica-based coating may require active control of gas chemistry in order to eliminate oxide volatility concerns, as SiO equilibrium pressure decreases with increasing O_2 (H_2O).

The inherent weakness of a coating based on SiO_2 formation is oxide volatility in low oxidizing ambients. This volatilization is a direct result of the thermodynamics of the Si-O system, primarily the Gibbs free energy of formation for SiO_2 . An obvious conclusion one can draw from a thermodynamic analysis is it would be preferred to use an oxide system with a larger (negative) Gibbs free energy of formation. Typically a more negative free energy of formation indicates stability and a greater resistance to volatilization. As the Ni-base superalloy coating review demonstrates, aluminum-base coatings are the pre-eminent environmental barrier coating technology and the most widely used oxide forming barrier. A thermodynamic analysis of the Al-O system reveals a more stable oxide former as compared to Si. Figures 8a and b are volatility diagrams for the Al-O system plotted against the H_2O/H_2 fraction similar to the previously described silica diagrams (orange boxes indicate typical HTGR water/hydrogen fractions). Because Al_2O_3 has a large, negative Gibbs free energy of formation, the amounts of volatile oxides in equilibrium with the solid phases are very small. At 900 K, only 10^{-32} atmosphere of $Al(g)$ must be produced to maintain equilibrium with solid Al_2O_3 ; at 1420 K, this pressure is 10^{-15} atm. These low pressures signify extremely slow recession rates. Figure 9 plots recession rate for Al_2O_3 as a function of temperature in meters per minute, as well as cumulatively over the proposed reactor lifetime. At 1420 K, the Al_2O_3 recession rate is about 0.0001 Å/min. At this rate, it will take the entire reactor lifetime to sacrifice 0.1 μm of Al_2O_3 to volatilization. However, this does not mean that there cannot be coating loss due to other processes like erosion under high He flow rates, but it does mean that oxidized aluminide coatings offer a distinct stability advantage over silicide coatings.



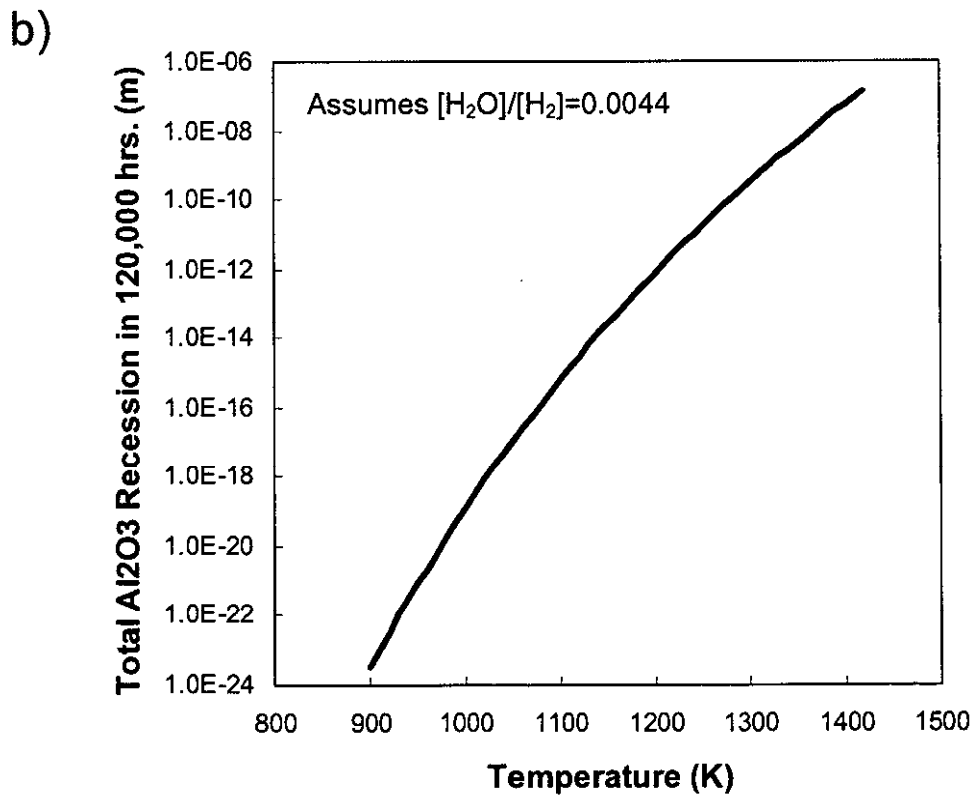
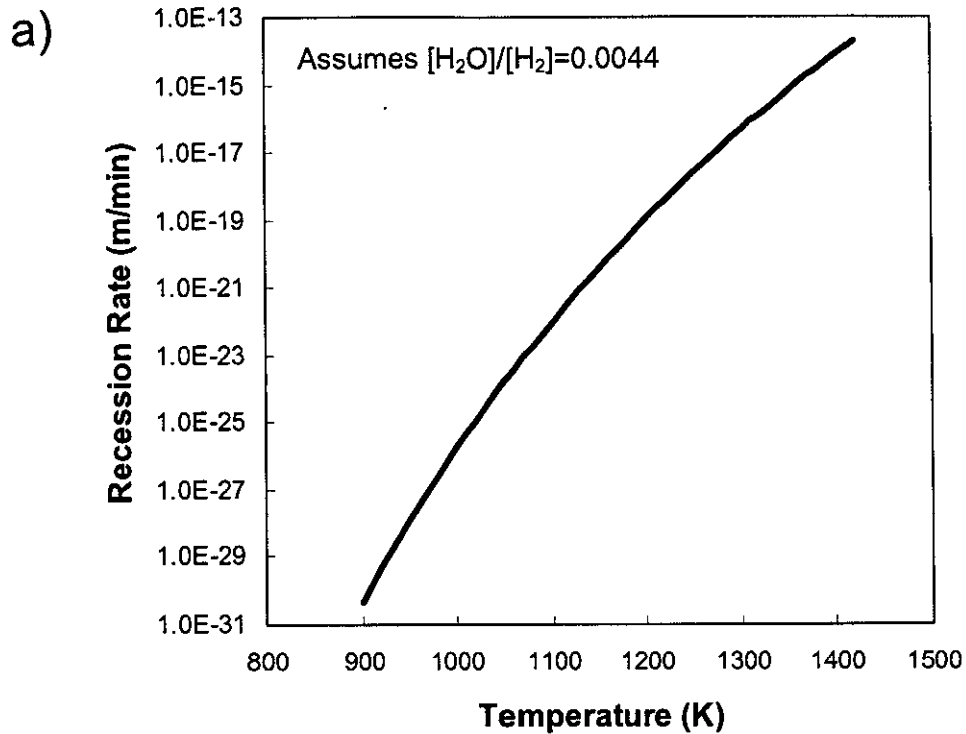


Figure 9. a) The estimated effect of temperature on recession rate for alumina, assuming a $[H_2O]/[H_2]$ fraction of 0.0044, and b) the resultant alumina recession in 120,000 hrs. Recession expected with Al_2O_3 for a Prometheus application is insignificant.

Ir/Re-based Refractory Metal Alloy Protection:

The second method upon which attention has been focused for protection of refractory metals is the Ir/Re duplex coating system. These coatings have been exclusively used in extremely high temperature rocket nozzles where there is a very aggressive, oxidizing environment.[58] This may be notable as the one protection scheme reviewed here that does not rely on formation of a passive oxide.

Iridium resides among the platinum metals group in the periodic table due to its oxidation resistance. Thermodynamic information for the Ir-O system is scarce, but data available for the gaseous oxide IrO_2 (that forms above 1373 K) demonstrates it is endothermic.[59] This increases the attractiveness of Ir as it will not be able to reduce H_2O or CO and form this volatile oxide (CO and H_2O being exothermic are very stable in comparison to volatile IrO_2). Any volatile Ir-oxide formation will be limited to that which reacts with free O_2 , which is available in very small quantities only. If one makes similar assumptions as before regarding the ratio of $\text{H}_2\text{O}/\text{H}_2$, at 1420 K the amount of free O_2 (strictly based on a thermodynamic balance with H_2 and H_2O) will be approximately 10^{-17} atm, therefore volatile oxide formation will not be a concern. Solid IrO_2 , which forms below 1373 K, has been described as stable and very slow growing. IrO_2 has a negative Gibbs free energy of formation below 1373 K, but is not more negative than water or carbon dioxide.[60] As a consequence, solid IrO_2 will also rely on reaction with pure O_2 to form, and therefore Ir will likely not participate in any substantial oxide formation.

In general agreement with the above discussion, data from open literature sources suggest that loss of Ir due to recession from volatile oxide formation or from direct metal sublimation is extremely low. Figure 10 is a plot of recession rate for Ir in oxygen as a function of pressure and temperature. These data reveal a recession rate of approximately 1 Å/sec at a temperature of 2238 K [61], which is over 800 K hotter than maximum planned temperatures for the Prometheus reactor core. At 1420 K, the recession rate would be expected to be negligible based on these data. Equilibrium vapor pressure of Ir, calculated from available thermodynamic data,[62] is plotted in Figure 11 as a function of temperature. The data demonstrate that Ir is very stable within the proposed core temperature range. Based on the high melting point of Ir and its thermodynamic reluctance to form oxides, recession is not expected to be a limiting factor. However, based on the long operating times that would be required from any coating in the Prometheus reactor, experiments should be conducted to measure oxide growth throughout the proposed temperature range.

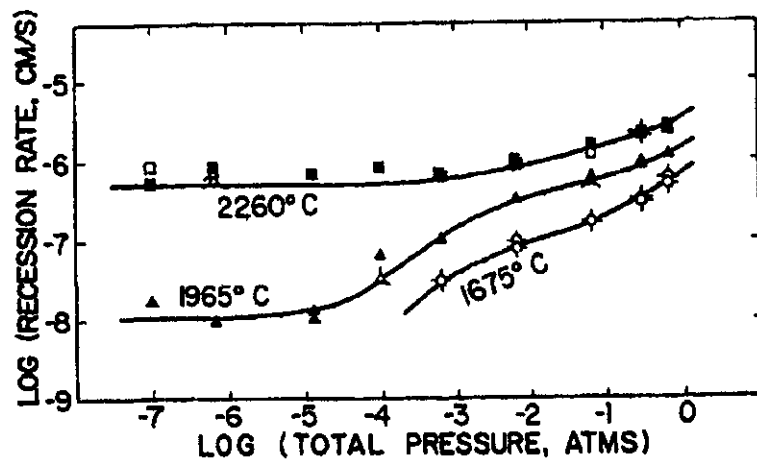


Figure 10: Experimental results showing the recession of Ir in air at different temperatures [61]

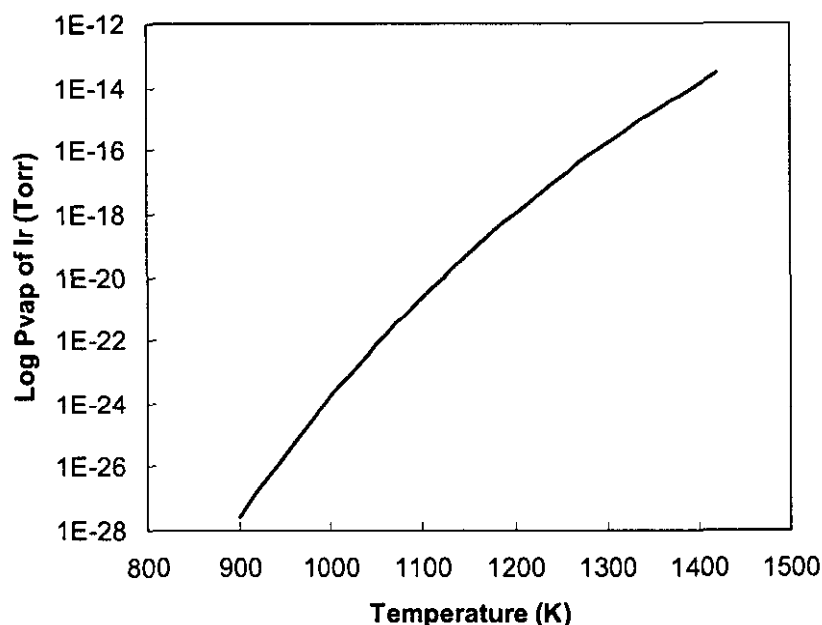


Figure 11: The equilibrium vapor pressure of Ir as a function of temperature. Preliminary design specifications call for a core operating temperature between 900 and 1420 K. Calculated from thermochemical data [62]. For the proposed Prometheus thermal range Ir is very stable.

A possible limiting factor for Ir is its diffusivity and metallurgical stability with Re and other refractory metal alloys. Ir demonstrates mutual solid solubility with all of the refractory metals (Nb, Ta, Mo, W, Re) that are under consideration for cladding and/or core structural materials. For binary alloys of Ir and Nb, Ta, Mo, or W, there is significant solubility (~5-20 at.%) in terminal solid solutions, and 4-5 intermetallic phases present in each binary system (see Figure 12). There are also limited data to suggest that interdiffusion is fairly rapid: for Ir-Ta diffusion couples held at 1473 K for 4 hours, a diffusion zone thickness of 4 μm was measured.[63] Caution is therefore warranted in coating Ir directly on a refractory metal alloy for fear of rapidly forming brittle intermetallic phases and weakening the coating/substrate interface.

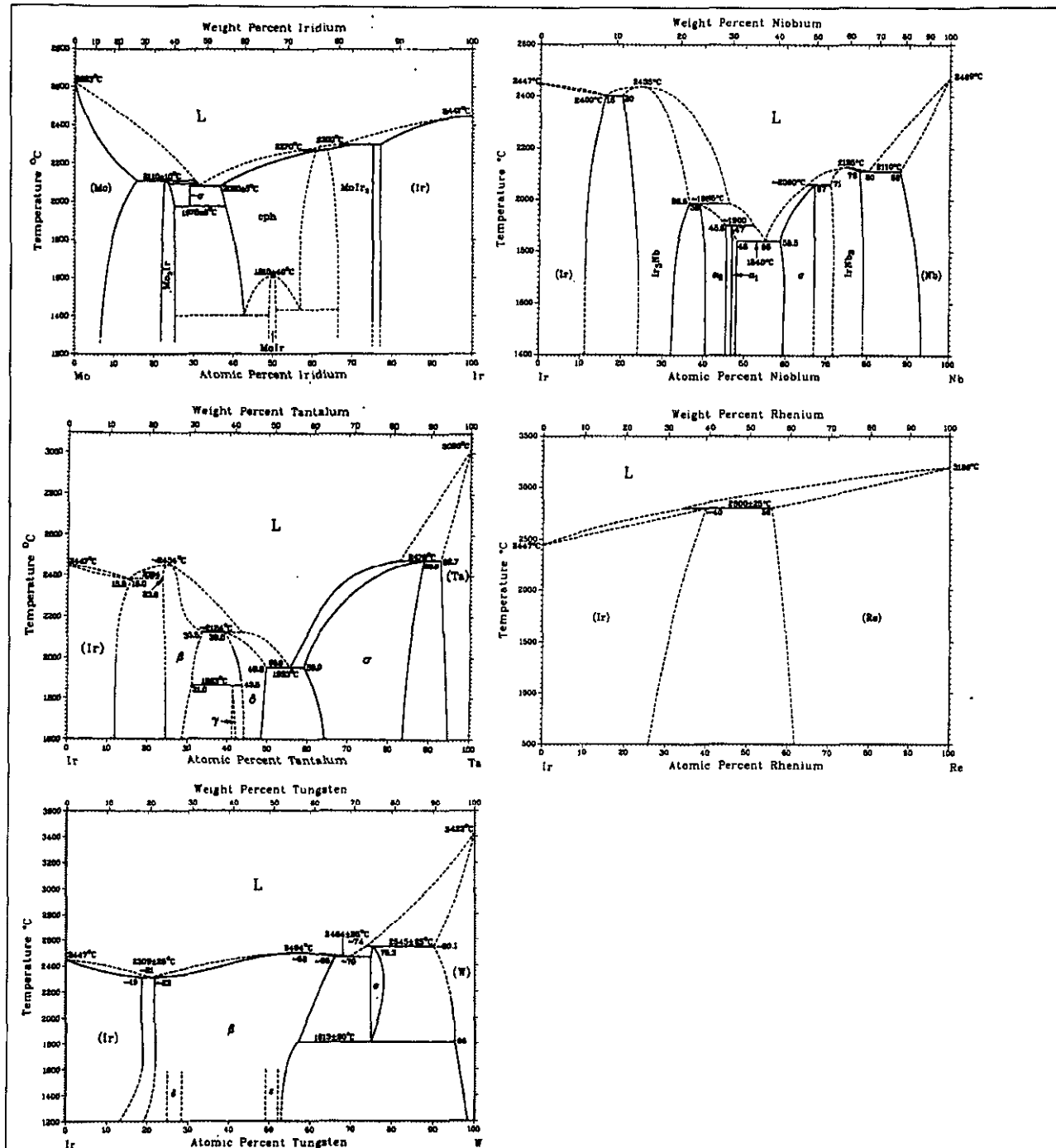


Figure 12: Binary phase diagrams of Ir with the various refractory metals. Of this group, Ir-Re is the only system that does not form intermetallic phases.[35]

The effect of dissolved Ir on refractory metal alloy mechanical properties is unknown. The sole literature source that suggested use of Ir/Re for oxidation protection on a Ta alloy claimed the need for Re as a diffusion barrier between Ir and Ta. Re is the only refractory metal that does not form an intermetallic phase with Ir, but both terminal solid solutions display very large solid solubility (25 at.% Re in Ir and 40 at.% Ir in Re). While eliminating potentially detrimental phase formation, excessive solubility may prevent Ir from successfully protecting Re if there is sufficient diffusivity and Re can reach the coating surface.

There are very little available diffusion data for the Ir-Re system. The only report available at the time of this writing was published by Reed et al. at the NASA Lewis Research Center.[64] Their results indicate Re is the fast diffusing species with an activation energy of 1.23 eV, strongly indicative of a grain boundary diffusion mechanism (see Figure 13). At the lowest envisioned core temperature for Prometheus (900 K), the average diffusion length given by an $x \approx \sqrt{Dt}$ approximation yields a value of 13 μm (0.5 mil) over a lifetime of 120,000 hours. This means an Ir layer would need to be greater than 13 μm to prevent any Re from reaching the Ir surface. At the highest proposed core temperature of 1420 K, diffusion distance increases to 241 μm (9.5 mils). This thickness may be prohibitively large based on neutronic and mass concerns. To prevent any oxidation of Re at this temperature, Ir would need to be thicker than 241 μm , and Ir has a density of 22.65 g/cm³. For a 241 μm thick coating of Ir, every square centimeter would add 0.55 gram to the total reactor mass. Based on preliminary design data with a cladding surface area of ~204117 cm², the necessary Ir would add 111 kg to reactor mass.

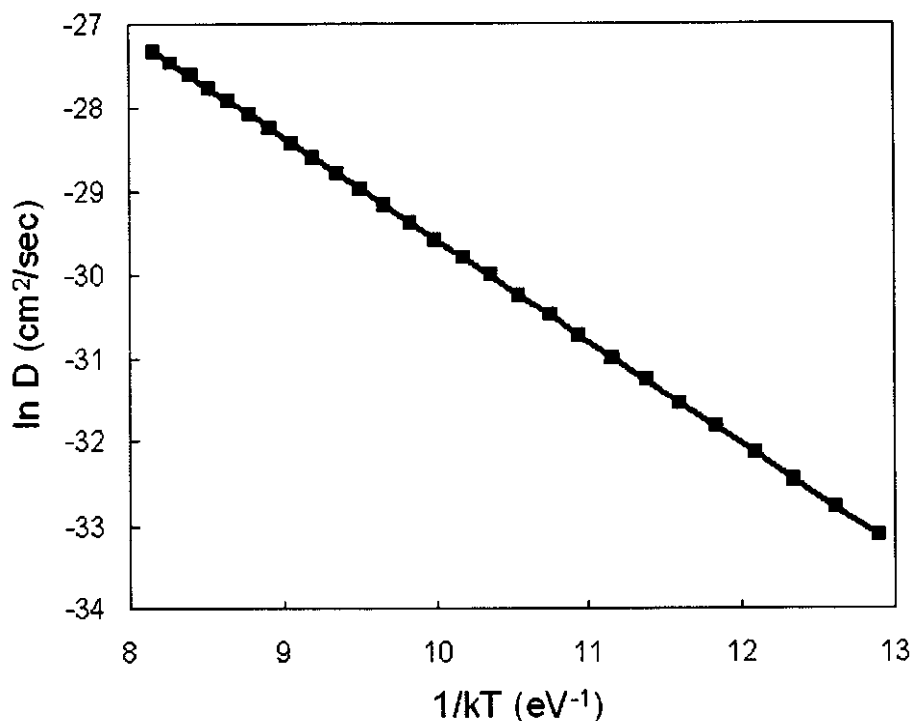


Figure 13: Interdiffusion data from Ir-Re collected from 1673-2173 K and extrapolated downwards to the 900-1420 K range. [64]

The interface between Re and any refractory metal alloy must be evaluated for metallurgical stability. As well as having significant mutual solid solubility, Re forms intermetallic compounds with all other refractory metals (W, Mo, Ta, and Nb). A detailed NASA-sponsored study of interdiffusion between Re and Ta, W, Nb, and Mo demonstrated intermetallic phase formation in interdiffusion zones of all Re-refractory metal diffusion couples.[65] Cracks were often observed in Re-Nb and Re-Ta couples, while cracks in the Re-Mo and Re-W couples formed only after long times at 2273 K. In addition to phase formation, interdiffusion zone thickness as a function of temperature and time was presented (see Table 3, for t=120,000 hrs).

Table 3: Calculated interdiffusion zone thickness for refractory metal couples based on a time of 120,000 hours. [65]

Diffusion Couple	900 K (m)	1420 K (m)
Nb/Re	4.2×10^{-9}	3.2×10^{-5}
Ta/Re	2.1×10^{-8}	2.6×10^{-5}
W/Re	2.4×10^{-9}	1.1×10^{-5}
Mo/Re	1.6×10^{-7}	7.4×10^{-5}

At 900 K, interdiffusion zone thickness between Re and other refractory metals is on the order of nanometers, while at 1420 K, diffusion results in tens of microns of mixed material. This would create a situation where Re is being depleted via diffusion into, and reaction with, the underlying refractory metal alloy component. Interactions between Re and refractory metal alloys are a concern, particularly in Mo-Re where excess Re would drive formation of the deleterious σ phase.

Rapid diffusion at elevated temperatures increases the required mass of Re necessary to separate Ir and any refractory metal alloy. Due to relatively large neutron capture cross-sections in Ir and Re (420 and 89 Barns, respectively)[66], Ir and Re would act as poisons and necessitate additional fuel. To successfully extend Ir/Re for the long times proposed for the Prometheus reactor, diffusion of Re through Ir must be reduced, either through alloying or altering coating microstructure. It must also be determined whether it is better to have one diffusing interface between Ir and refractory metal alloy, or two interfaces, one for Ir/Re and one for Re and the refractory metal alloy. Neither situation is desirable based on long-term stability requirements.

SiC Protection:

Maintaining stability of SiC in a lightly-oxidizing He Brayton reactor will have many of the same issues as SiO₂. If a SiC core is actively oxidizing it will act as an oxygen and water scavenger, much like a graphite core does in current HTGRs, with the exception that SiO will be formed concurrently with CO. For SiC/SiC composites, there is an additional concern over stability of the material used to form the weak interface between fiber and matrix. BN is typically used as this interphase material, and it will also readily oxidize and volatilize.[67] Increases in CO will come from conversion of CO₂, H₂O, and O₂ with the result that the Brayton working fluid will become reducing and carburizing as ratios of CO:CO₂ and H₂:H₂O increase. As this occurs, not only will SiC be suffering from active oxidation and recession, but any uncoated Ni-base superalloy exposed to the gas loop could have its native Cr₂O₃ layer stripped away and then suffer rapid carburization or decarburization. However, if the SiC is passivated with a SiO₂ surface layer or other oxide former coating, its ability to scavenge oxygen will be diminished and the atmosphere will be more oxidizing and therefore more congenial to the formation of passive oxides on superalloy components.

Protection of SiC has already been highly engineered (a great deal of which was done at NASA-Glenn) because it is targeted for future gas turbine applications and must survive a very aggressive fuel/oxidizing environment. The internal flow path of a Brayton reactor would not have the same aggressive oxidative and corrosive environment, but would suffer from ceramic instability, similar to a silicide coating, as described above in the refractory metal alloy section. All multilayer coatings for SiC that have been investigated by NASA have SiO₂ as a major constituent at each coating level. Based on the thermodynamic analysis provided earlier,

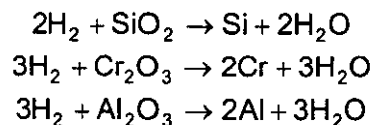
stability of SiO_2 in a He-driven Brayton engine for long times is questionable above ~ 1100 K. Because water-based corrosion is not a concern, perhaps the correct path forward is to design a new protective coating, rather than trying to adapt what has previously been done by NASA and the aerospace industry.

Due to the high-temperature instability of Si-based ceramics, a primary requirement for protection of SiC in impure He would be elimination of Si-O volatilization. This can be accomplished either through controlling gas chemistry and creating a situation where SiC self-passivates, or by coating SiC with an EBC. A coating that would form a continuous layer of Al_2O_3 on the exposed surface would be the preferred method. However, as Al is a more reactive element than Si, it is unlikely that a MCrAlY or aluminide coating directly placed on SiC would provide acceptable protection. Al in intimate contact with SiC will react to form mixed silicon-aluminum carbides.[68] This literature review would suggest development of a multilayer coating with a base coat to provide CTE matching like mullite, and a reservoir top coat that would provide Al to form a continuous Al_2O_3 scale on the exposed surface.

Superalloy Protection:

Chromium-containing Ni-base superalloys generally obtain oxidation resistance through selective oxidation of Cr to form an external protective film of Cr_2O_3 . However, degradation of Cr_2O_3 occurs from $\text{CrO}_3(\text{g})$ volatilization at high temperatures and high oxygen pressures, and Cr volatilization at low oxygen pressures. Primarily because of high oxygen pressure volatility, MCrAlY coatings were developed to make use of the more stable Al_2O_3 within an aggressive gas turbine environment.

For the He Brayton reactor under consideration, there will not be a highly aggressive oxidizing environment present to create volatile CrO_3 , but volatility of Cr will remain an issue. Figure 14 is the volatility diagram for the Cr- Cr_2O_3 system at 1150 K, the proposed upper design temperature for a superalloy turbine wheel. As with the similar Al and Si analyses, the orange box within the diagram represents a typical HTGR gas chemistry. At this chemistry and temperature, equilibrium vapor pressure for Cr is 10^{-12} atm, a value too large to guarantee stability over the proposed mission lifetime. However, of greater concern for reliance on Cr_2O_3 for protection is its chemical stability in contact with the gaseous H_2 and H_2O impurities. As the ratio of $\text{H}_2:\text{H}_2\text{O}$ increases in the vapor phase, an environment becomes more reductive and can reach a point where metal oxides become unstable. Onset of degradation, along with required $\text{H}_2:\text{H}_2\text{O}$ ratios are functions of the Gibbs free energy of formation of the metal oxide in question. A more negative free energy of formation indicates a greater resistance to hydrogen reduction. Figure 15 demonstrates this trend for three different metal-metal oxide systems by plotting ratios of $\text{H}_2:\text{H}_2\text{O}$ that lead to equilibrium, as a function of temperature. The three plotted reactions are:



These lines demarcate metal and metal oxide phase stability regions, where metal is stable in its elemental form above a line, and underneath metal oxide is the thermodynamically favored phase. The dashed line in this figure represents the approximate background $\text{H}_2:\text{H}_2\text{O}$ ratio reported in HTGR literature. At ~ 980 K the equilibrium curve for Cr crosses this prototypical HTGR line, creating a reductive atmosphere with respect to Cr_2O_3 . The threshold for Cr_2O_3 reduction is within the proposed operational temperature range for a superalloy turbine wheel (700-1150 K). This would lead to corrosion of any protective Cr_2O_3 layer leaving any superalloy

component open to further environmental attack by impurities within the He working gas. While SiO_2 is stable with respect to hydrogen reduction throughout this entire temperature range, it does suffer from volatilization losses at reduced oxygen pressures as previously discussed. Based on its large, negative free energy of formation, Al_2O_3 once again demonstrates its stability with respect to a high-temperature, impure-He environment.

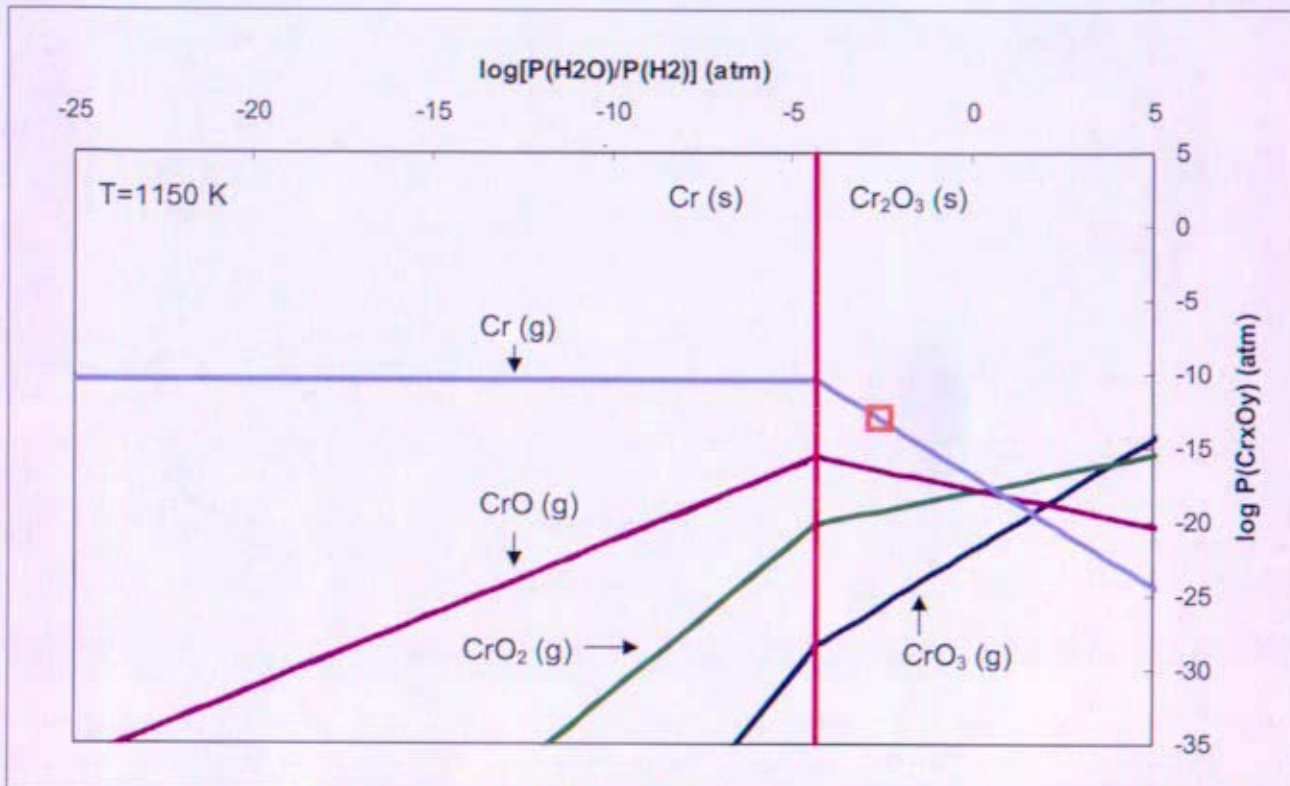


Figure 14: Cr-O volatile species at 1150 K. Orange box represents the typical $[\text{H}_2\text{O}]/[\text{H}_2]$ fraction measured in HTGRs.

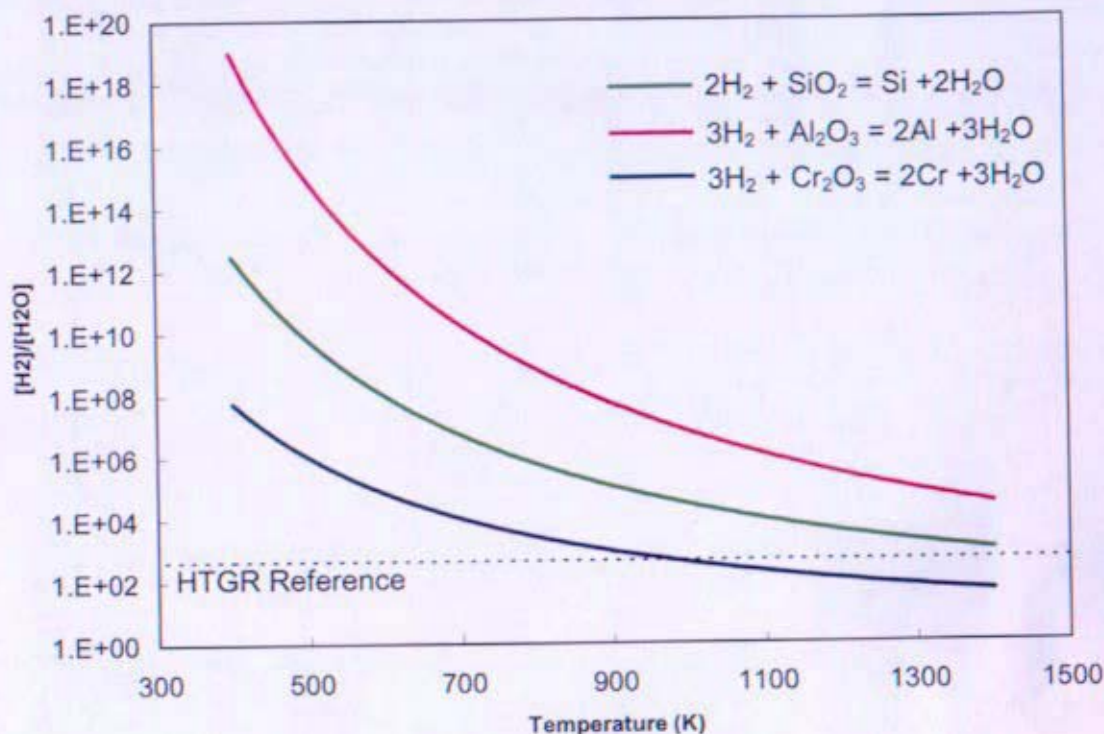


Figure 15: Metal/oxide stability diagram with respect to $[H_2]:[H_2O]$ for Al, Cr, and Si. Above a colored line the base metal is the thermodynamically favored phase, while below the oxide is stable. The dashed line represents a typical hydrogen-to-water ratio observed in HTGRs.

A major requirement for use of Ni-base superalloys is the maintenance of their carbon activity with respect to an impure-He gas. If a superalloy is exposed to a decarburizing environment with sufficient thermal energy, any carbides present in the alloy will dissociate to yield up carbon to the He gas, thereby compromising creep strength, and putting any refractory metal alloys in the gas loop at risk for interstitial embrittlement. Conversely, if ambient gases become highly carbon-rich, there is a risk that Ni-base superalloys can rapidly carburize and become embrittled. It has been shown in HTGR literature [69][57] that reduction of Cr_2O_3 by hydrogen to form water is the first step in this process. Whether an unprotected superalloy will carburize or decarburize is dependent on the $CH_4:H_2O$ ratio present within the He, but loss of protective chromia exposes superalloys to attack.

Ultimate gas chemistry will be a function of all the materials (and their associated temperatures) in contact with the He gas loop, and whether materials are passivated or actively oxidizing/reducing. In particular, the chosen core material will play the biggest role in how impurity content of the He gas develops. An uncoated refractory metal alloy based on Nb or Ta would likely act as a carbon getter and cause decarburization of any superalloy that is hot enough to support outward diffusion of carbon. An uncoated SiC core that is actively oxidizing would create a spectrum of impurities similar to an HTGR [67] and could cause carburization or decarburization depending on the final impurity contents. A passivated SiC core, either through passive oxidation or through coating, or a coated refractory metal alloy core would likely do little to add to, or subtract from, the gaseous carbon content. This situation could be detrimental if the carbon content of the gas is not sufficient to maintain carbon levels within exposed superalloy material. Because the exact chemical concentrations of impurities is not known *a priori*, it is

appropriate to select a coating system for hot superalloy components that can withstand a variety of possible environments.

Environmental protection for superalloys is a highly mature technology. Coating materials are very well known and would require little to no development. The primary issue that needs addressing is coating application. For MCrAlY coatings in turbines, the typical application route is thermal spray. This is not possible for coating the insides of long, complex shaped piping. The only two coating methods that could work in this situation are pack cementation or atomic layer deposition. ALD is not a practical solution because it is not amenable to the growth of pure metals and is inherently slow. Pack cementation may be used for aluminizing and chromizing, but addition of a reactive element (Y or Hf) and other alloying elements for a simultaneous growth would require investigation. It would be necessary to determine how to control coating stoichiometry based on the stoichiometry within the pack, and even if these can be simultaneously grown. Based on current state-of-the-art coating technology, pack cementation is likely the only method for coating an alumina-former system inside long, serpentine tubing.

6. Proposed Experimental Work

Prior to any experimental work on specific coating systems, the following parameters need to be defined:

- Specific structural materials need to be selected. Type of materials present will determine the degradation mechanisms that will dominate and how impurities in the gas phase will evolve.
- A prototypical impure-He environment needs to be defined. Gas impurity concentrations need to be determined to at least the order-of-magnitude in order to evaluate the level of interaction that exist between selected structural materials.
- Operating temperatures need to be specified. Coating stability will be strongly dependent on temperature. In the case of Ni-base superalloys, coatings may not be necessary if the temperature is low enough.

The following issues need to be addressed with experimental programs, dependent on a core/cladding material selection:

Silicides-Refractory Metal Alloys

- Mass-loss measurements from silicide-coated refractory metal alloys need to be performed within a prototypical impure-He environment, *and within the presence of a prototypical mass and surface area of superalloy to act as a chemical source of interstitials.* Initial emphasis should be placed on R512E (Si-Fe-Cr) because of its proven track record and availability, but a survey should be taken of all proprietary silicide coatings available from industrial sources.
- Coating stability must be measured for silicide coatings in the as-deposited state as well as coatings that are pre-oxidized prior to insertion within an impure-He environment to address the issue of peeling.
- Coated test specimens should be in shapes appropriate for mechanical testing so that mechanical properties can be measured following environmental testing (similar to proposed capsule testing for the refractory metal alloy/superalloy mass transport research).

- Microstructural data from post-test samples will be necessary. Of particular importance will be quantification of interdiffusion and reaction between silicides and refractory metal alloys. Questions to be addressed are:
 - Is there significant interdiffusion between the silicide and refractory metal alloy?
 - How rapid is the interdiffusion (kinetics)?
 - Is there any phase or void formation?
- Resistance to spallation under thermal cycling must be measured. While it is not planned to subject Prometheus to multiple thermal cycles, an understanding of coating durability would allow for design flexibility.
- Ability for the coating to heal cracks should be measured in an impure-He environment. Silicide coatings are known for this property, but it is unclear whether this healing can occur without oxygen.

Aluminides-Refractory Metal Alloys

- Diffusion rate of Al into any selected refractory metal alloy must be measured (or determined from a literature search).
- Scoping tests should be carried out to determine if there are any effective barrier materials that can be used to prevent or significantly slow interdiffusion between an aluminide coating and a refractory metal alloy. Suggested diffusion barriers are Al_2O_3 , MgO , ZrO_2 , HfO_2 , BeO , Y_2O_3 , and ThO_2 , based on their thermodynamic stability with respect to Ta, Nb, Mo, and W.
- Based on diffusion barrier scoping test results, long term testing should be carried out within a prototypical impure-He environment
- Post-testing microstructural analysis will be required to address:
 - Quantification of interdiffusion between coating and substrate
 - Characterization of any interfacial phase formation
- Resistance to spallation under thermal cycling should be measured. While it is not planned to subject Prometheus to multiple thermal cycles, an understanding of the coating durability would allow for design flexibility.
- The ability for the coating to heal cracks should be measured in an impure-He environment.

Ir/Re-Refractory Metal Alloys

- Diffusion couples of Ir and any selected refractory metal alloy should be produced and tested to determine interdiffusion zone thickness and phase(s) of any reaction products. This data should be compared to pre-existing data for Re and the same refractory metal alloys to determine if addition of a Re diffusion barrier is necessary or useful.
- Volatile-oxide mass-loss from exposed Re only becomes an issue if there is sufficient oxygen available. Therefore, oxidation-induced mass-loss experiments must be conducted with Re in the SNPP impure-He environment to determine if the extra oxidation resistance of Ir is necessary.
- Interdiffusion in the Ir-Re system needs to be quantified. This will identify thicknesses of Re necessary to prevent Ir interaction with a refractory metal alloy substrate. The thickness of this system is critical due to its relatively high mass (as compared to the oxide formers), and neutron absorption cross-section.
- Should a required thickness be deemed reasonable, mass-loss/gain measurements need to be taken from samples placed within a prototypical impure-He environment in the presence of a prototypical mass of superalloy to act as a chemical source of interstitials.

- Coated test specimens should be in shapes appropriate for post-exposure mechanical testing.
- Post-testing microstructural analysis will be required to address:
 - Is there significant interdiffusion between Re and the refractory metal alloy substrate?
 - How rapid is interdiffusion?
 - Is there phase or void formation?
- Resistance to spallation under thermal cycling should be measured. While it is not planned to subject Prometheus to multiple thermal cycles, an understanding of the coating durability would allow for design flexibility.
- Ability for the coating to heal cracks should be measured in the impure-He environment. At the maximum proposed core temperature of 1420 K, Ir would be at a homologous temperature (T/T_{melt}) of 0.5 and there may be enough diffusion within Ir to seal cracks. At 900 K, $T/T_m=0.33$ and sealing of cracks is less likely.

SiC

- Mass-loss measurements from SiC need to be performed within a prototypical impure-He environment. These tests should be conducted with both as-grown SiC and with pre-oxidized SiC. This will provide a baseline for the losses due to volatility.
- Fully-crystallized, mullite-coated SiC should be tested for weight gain/loss within the impure-He environment to determine if mullite alone is sufficient to protect SiC.
- Should mullite alone prove insufficient, a topcoat of yttria-stabilized-zirconia, or hafnia can be applied. NASA results indicate these are effective in the absence of many thermal cycles.
- Deposition of aluminides onto mullite should also be investigated as an aluminum reservoir system would be the ideal EBC.
- Resistance to spallation under thermal cycling should be measured. While it is not planned to subject Prometheus to multiple thermal cycles, an understanding of the coating durability would allow for design flexibility.

Ni-base Superalloys

- Formation of a protective MCrAlY coating on the inner surface of a superalloy tube of serpentine nature will require a coatings development project. Experiments must be conducted to determine proper growth parameters necessary to deposit a coating of desired stoichiometry, as thermal spray will not be possible. Coating a Ni-base superalloy pressure vessel could likely be accomplished via a thermal spray technique.
- When growth conditions have been established, material testing can be conducted in a similar fashion to the above listed situations. Mass-loss/gain measurements must be taken within a prototypical impure-He environment, *and in the presence of a prototypical mass and surface area of core material* (refractory metal alloy or SiC).
- Coated test specimens should be in shapes appropriate for post-exposure mechanical testing.
- Post-testing microstructural analysis will be required to address:
 - Carbon loss/gain from the superalloy and subsequent phase evolution.
- Resistance to spallation under thermal cycling should be measured. While it is not planned to subject Prometheus to multiple thermal cycles, an understanding of the coating durability would allow for design flexibility.

7. Conclusions

A great deal of protective coating research has been conducted for use with SiC, Ni-base superalloys, and refractory metal alloys. In all cases, research has focused on how to protect structural materials from extreme temperatures under highly oxidizing ambients, conditions that are not representative of the proposed Prometheus SNPP. It is not evident that the available technologies for any of the candidate materials are directly applicable in the Prometheus application, and substantial development and testing will be required for optimization of coatings for all the material classes in the anticipated environment of the Prometheus system.

Thermodynamic modeling indicates that coatings for protection of superalloys based upon formation of a protective Al_2O_3 scale would be stable at all temperatures proposed for core and plant of the proposed Prometheus system, while stability of Cr_2O_3 formers at high temperatures is questionable. Additionally, Ni-base superalloy protective coating technology for use in air-breathing environments is very mature with a large vendor base to draw from. Thermodynamic analyses indicate that one or more of the currently available technologies may be viable for protection of Ni-base superalloys within Prometheus.

While at a more developmental stage, coating technology for SiC in air-breathing environments is available from an established vendor base. However, protection of SiC in the Prometheus environment will require further research to extend current technologies to atmospheres of lower oxidation potential or to develop new technologies optimized for the expected environment.

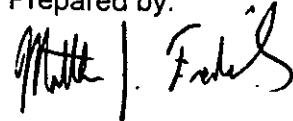
Long term protection of refractory metal alloys would require a substantial research and development effort. Existing coating technologies for refractory metal alloys either may not have the necessary high temperature stability (SiO_2 forming compounds), or may have prohibitively large neutron absorption cross-sections. However, the low oxygen and carbon potential environment anticipated in the Prometheus system presents a different but serious challenge from that faced by prior efforts where protection in air or air-breathing propulsion environments was the objective. In order to adapt some or all of the existing technologies to an impure-He-Xe environment, materials testing will have to encompass both coating/substrate interactions and coating stability within low oxidation potential environments.

In summary, it is judged that existing EBC technology for protection of Ni-base superalloys may be sufficient for use in an impure He-Xe environment. The majority of existing coating technology for silicon carbide and refractory metal alloys may be of limited worth for service in the Prometheus system environment. At the least, extensive testing and evaluation of available coatings in prototypical Prometheus environments will be required to assess their potential applicability, and it is believed that substantial development, testing and performance verification will be a necessity for qualification of coatings for all classes of structural materials under consideration.

Acknowledgements

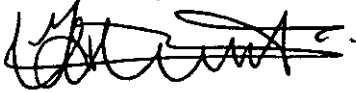
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Prepared by:



M. J. Frederick, Engineer
Space Structural Materials
Space Materials/MDO

Approved by:



Y. Ballout, Manager
Space Structural Materials
Space Materials/MDO

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